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RESEARCH AND DEVELOPMENT CENTER - SERVOMECHANISMS, INC.

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FINAL REPORT

Contract No. NObs - 86367

Project Serial No. SR-007-12-01

July, 1962

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LIST OF ILLUSTRATIONS

(continued)

I. INTRODUCTION

This is the final report covering the research study program which has been conducted by the Servomechanisms, Inc. Research and Development Center for the Bureau of Ships, Department of the Navy, on Contract No. NObs - 86367. The scope of this contract was a study of one method of thermoelectric application technique. Specifically, the work involved fabrication and test to investigate a method of structural encapsulation of washer-shaped thermoelectric elements under pressure.

One goal of the program was to verify preliminary evidence that thermoelectric elements are free from formation of mechanical cracks due to thermal shock, high thermal gradients, or thermal expansion problems when the thermoelectric material is held beyond its compressive yield strength. Thus, short path-length elements may be used with high thermal gradients, resulting in high electrical yield per kilogram of thermoelectric material with low degradation over long operating life. Under these pressure conditions, the requirement for matching the coefficients of thermal expansion of the thermoelectric elements to that of other structural materials becomes of only secondary importance. However, data on the chemical effects of various containment materials on performance was investigated. It was also intended to verify preliminary evidence that the use of high retaining pressures

will allow hot junction temperatures in excess of those which are normally practical by inhibiting the sublimation of critical fractions of the thermoelectric material, particularly under vacuum conditions. Another goal of the program was to verify that the method of producing the encapsulated washer-type elements would lead to low contact resistance within the generator.

During the course of the program, a number of experimental modules were constructed using this encapsulation technique, and life test data was obtained to establish the performance with time. These tests were run near 600° C. in a vacuum environment. A series of tests were also run on several of the test modules in which the heat input was turned off and on to give complete thermal cycling. The effects of containmnet pressure on semiconductor thermoelectric properties was also investigated.

These tests indicated that modules of this construction are capable of operating in vacuum at 600° C. for prolonged periods of time without serious degradation. The cycling tests indicated that this type module is capable of undergoing at least 2,500 start-up - shut-down cycles without any degradation. It was found that the thermoelectric properties of lead telluride were substantially independent of the applied retaining pressure and that good low resistance junctions could be formed and maintained by this pressure confinement. The test modules were fabricated with lead telluride as the active semiconductive

element, and no effort was made to obtain maximum efficiency since the major purpose of the program was to establish mechanical integrity during prolonged operation.

II. TEST MODULE DESIGN AND CONSTRUCTION

The thermoelectric units fabricated during the program to obtain test results were of a cylindrical design configuration. This form was chosen since it represents an optimum way of containing the thermoelectric material under the high compressive loads contemplated in the basic approach. It was also a geometry about which a great deal is known at SM/I, due to past experience with thermoelectric generators. Each test module consisted of one "P" and one "N" junction since this would give adequate test results. Lead telluride was used as the semiconductive material since a great deal is known about its mechanical properties and thermoelectric performance. The particular properties of lead telluride, such as low tensile strength and high coefficient of thermal expansion, are similar to those of other thermoelectric materials which might be considered. A thermoelectric test module following this design concept consists of two short cylindrical washer-like sections of lead telluride, one "N" type and one "P" type, cylindrically contained between metal inner and outer bands and separated by insulating washers. A complete test module of this type is one inch in diameter and is shown in the photograph in Figure 1. The design details are shown in the cross-sectional drawing of Figure 2. The containment pressure is supplied radially by the metal rings and longitudinal pressure was applied by exterior means through the Lavite anvils shown in Figure 2. The

Figure 1
Pressure Encapsulation
Test Module

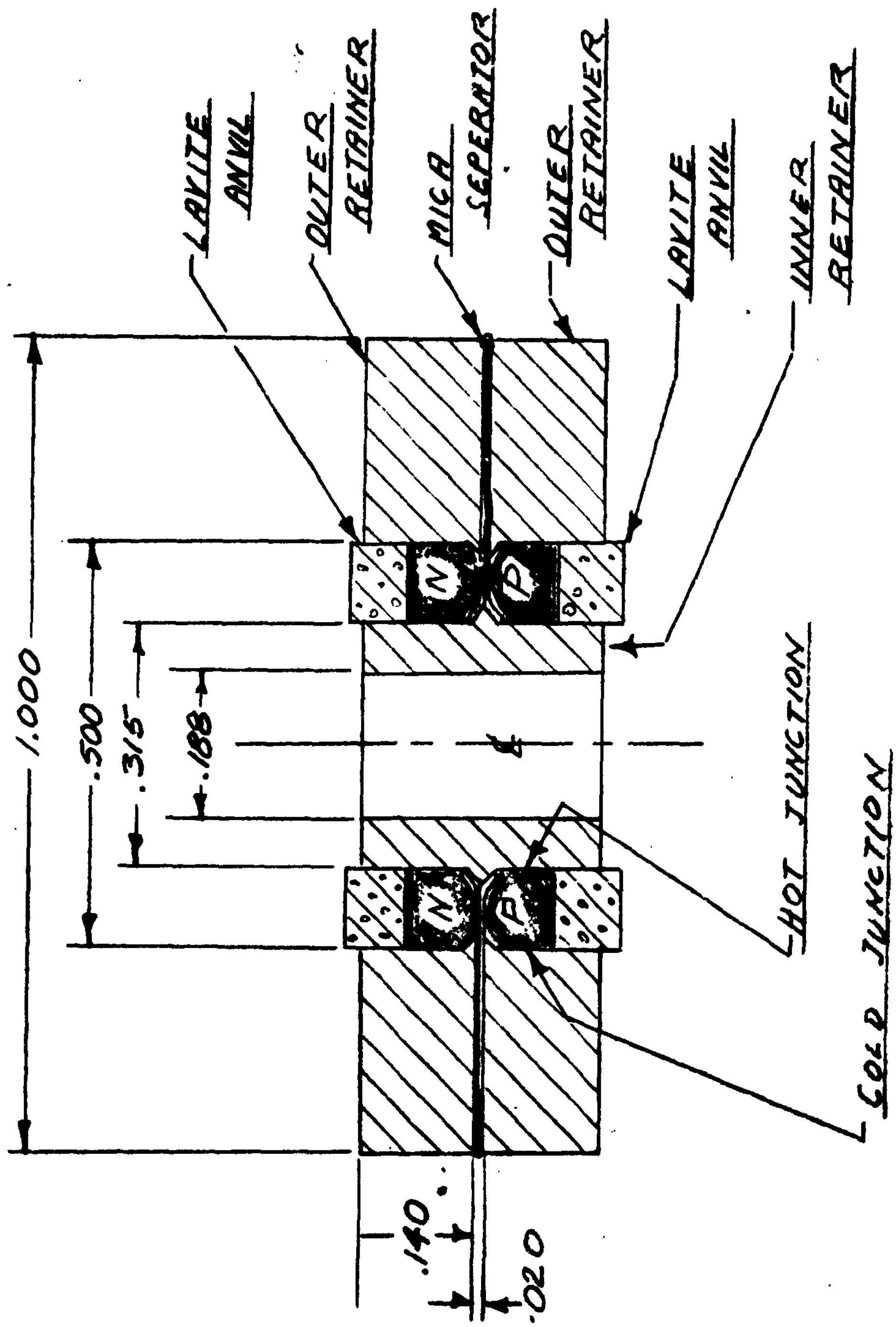

Figure 2

Standard Module

lead telluride circular elements are .5 inches o.d., .315 inches i.d., and .07 inches thick. Each contain one gram of lead telluride. This test module is a complete thermoelectric couple and may be tested individually to obtain the necessary performance data.

The "N" and "P" type lead telluride used in the fabrication of these modules was manufactured by Servomechanisms/Inc. following the procedures outlined in Appendix A. No efforts were made to optimise the thermoelectric properties of the material to obtain maximum efficiency since the scope of the contract was limited to mechanical fabrication and test.

The "P" and "N" type lead telluride, as manufactured, is in the form of a solid cast body. This material was crushed and ground and passed through a one hundred mesh screen to obtain a powder of controlled particle size. The powder was then cold pressed at approximately 60,000 psi in a mold having the proper dimensions to form solid bodies of the material. The resulting lead telluride bodies were then assembled, as shown in Figure 2, between the metallic inner and outer retaining bands with suitable insulation between the "N" and "P" type elements. These complete modules were then heat treated under pressure in an inert atmosphere on a definite time cycle to enhance thermoelectric properties.

The inner and outer retaining ring material was varied to determine possible interaction effects with the lead telluride under operat-

ing conditions. The materials investigated were ARMCO iron and two stainless steels, namely, AISI 416 and AISI 430 F. Basis for the selection of these materials was high creep strength at the operating temperatures, corrosion resistance, machineability, and chemical compatibility with lead telluride. High nickel containing alloys were avoided because of the known possibility of contamination of the lead telluride. However, the AISI 416 has a small amount of nickel content and was investigated to determine possible deleterious effects. The insulating material between the lead telluride wafers was varied to determine the effects of this factor on the life performance of this particular type generator configuration. The insulating materials investigated were mica, titanium dioxide, zirconium dioxide, and boron nitride. The latter three ceramic materials were introduced into the structure in the form of a cold pressed wafer formed from their powders.

III. TEST PROCEDURE

The test modules were evaluated in test chambers designed and constructed for this purpose. A four-station test stand was constructed to expedite the acquisition of life test data. A photograph of the test stand is shown in Figure 3. Figure 4 shows, in more detail, the layout of an individual station. Each station basically consists of an evacuated bell jar with provision for introducing variable compressive forces to the test modules. The pressure is applied by a means of two adjustable beam and fulcrum systems in cascade. The load of the calibrated spring seen on the left is reacted through a column in compression, which includes the radially restrained lead telluride elements of the module. In this way, the test module within the vacuum system may be subjected to a controlled and variable pressure of up to 50,000 psi, thus allowing investigation of performance as a function of pressure. The two halves of the compression column holding the module also provide an electrical path for the heating current. The hot junction temperature is introduced by electrical resistance heating of the inner cylindrical retainer of the test module. The power is supplied in the form of a heavy A.C. current which is provided by a transformer that is seen under the table in the photograph. The cold junction temperature is established by two water-cooled copper blocks which are spring loaded so as to provide good thermal contact with the cold junction radial retainers.

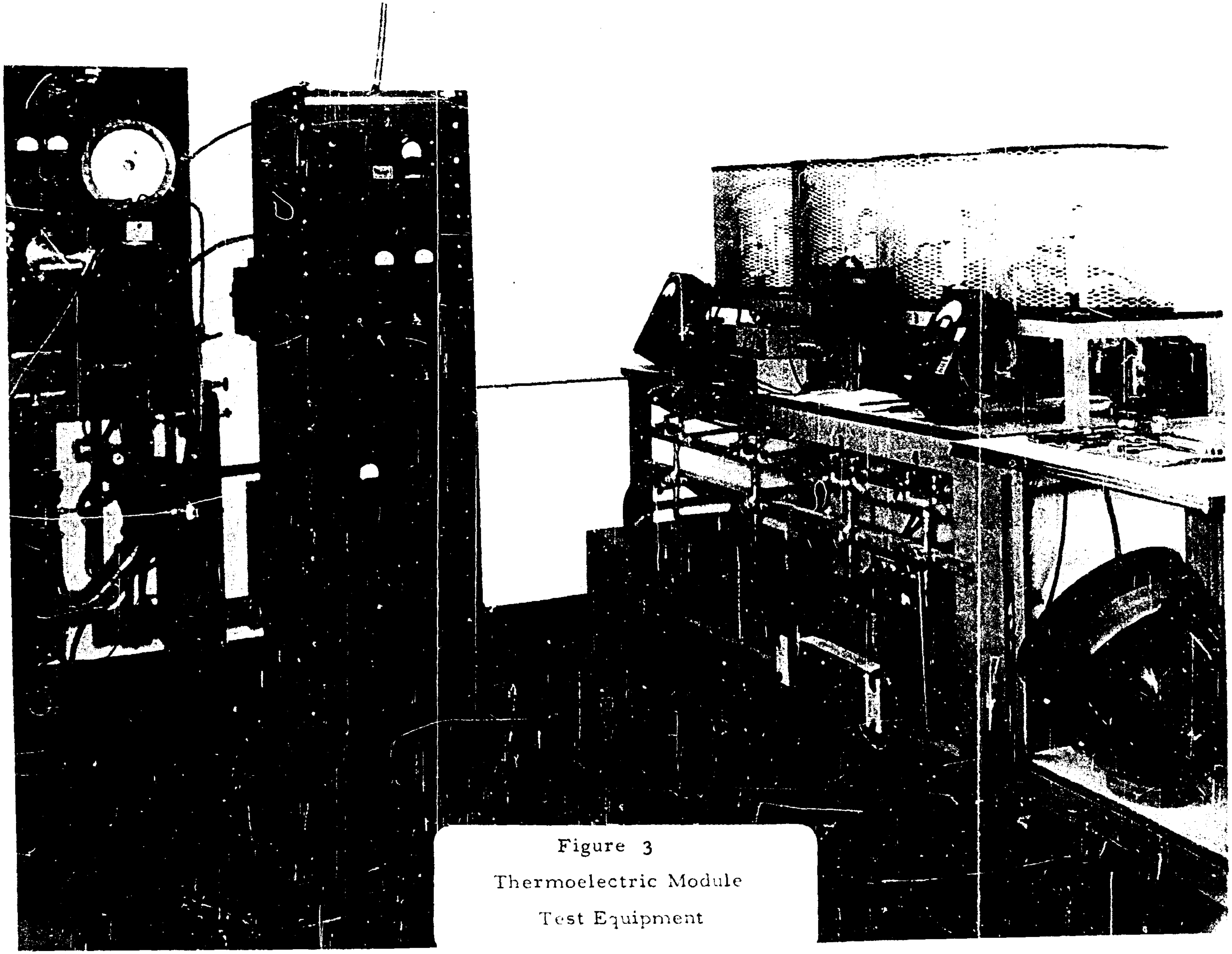

Figure 3
Thermoelectric Module
Test Equipment

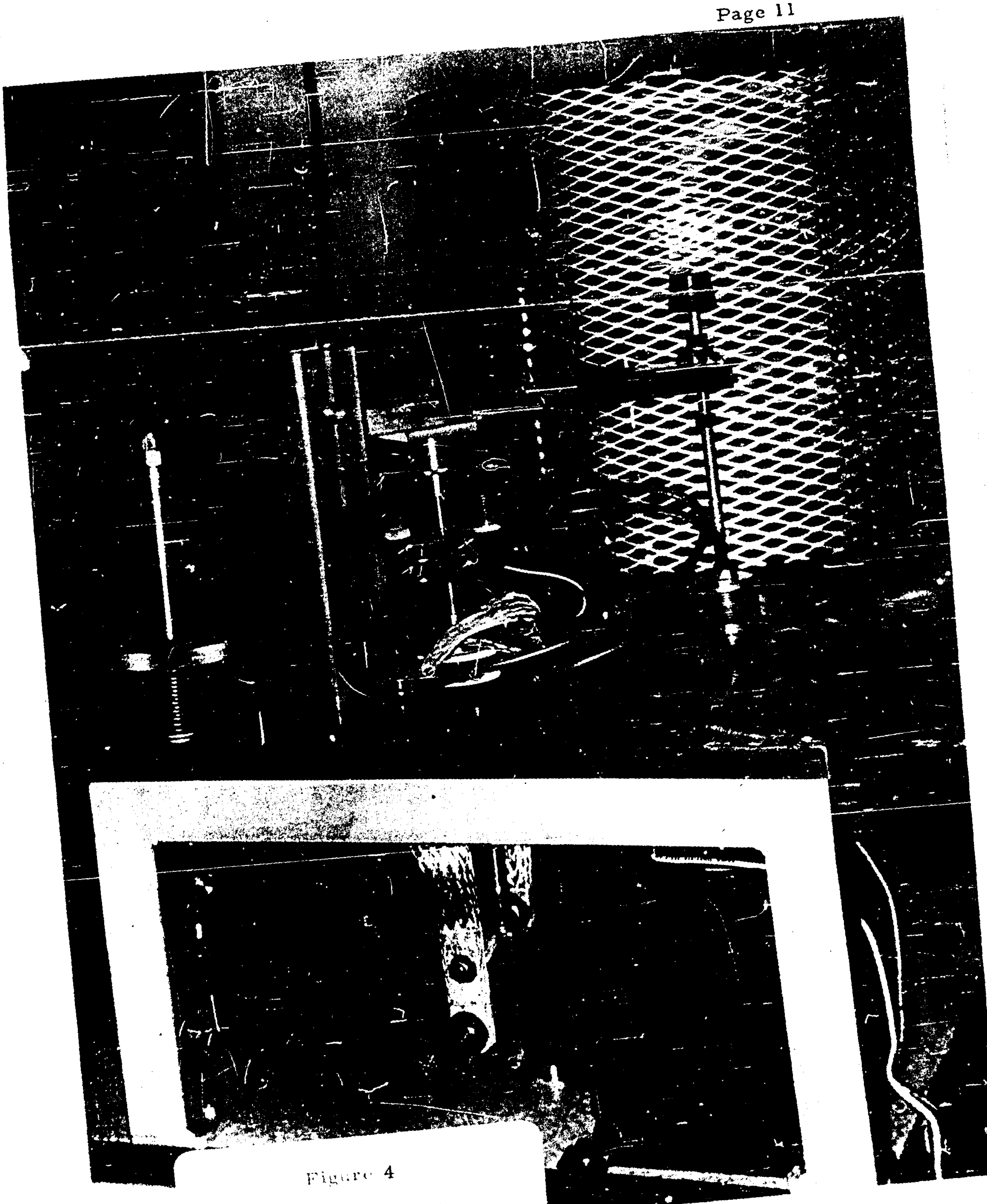

Figure 4

Test Stand Detail

The hot and cold junction temperatures are measured by means of chromel-alumel thermocouples. The output of the test module was computed by measuring the output voltage across a known resistive load. Provision is made for disconnecting the load to obtain the no load Seebeck voltage of the test modules. Operating data, such as internal resistance, power, output, efficiency, etc., are computed from these observations.

IV. TEST RESULTS

The following test results were obtained from the modules constructed on the program:

A. Life Tests

The test modules which were fabricated by the methods described previously were put on life test as early as possible in the program to get the maximum time span of test results. The following is the history of the modules during the course of the tests:

1. Test module # 1 was made using ARMCO iron as the retaining metal and used mica as the insulator between elements. The life test in a vacuum environment at about 10 microns pressure was conducted with hot junction temperatures in the range of 550° C. - 600° C. and a ΔT of 465° C. Figure 5 is a curve showing the performance parameters versus life under these conditions. At the end of 1,600 hours, the unit had experienced a 16% loss in power output and some decrease in the electrical conductivity. Most of the change in the performance occurred in the first 300 hours of life with little change after this point. The specific power output of this module was initially .73 watts per gram of active material.

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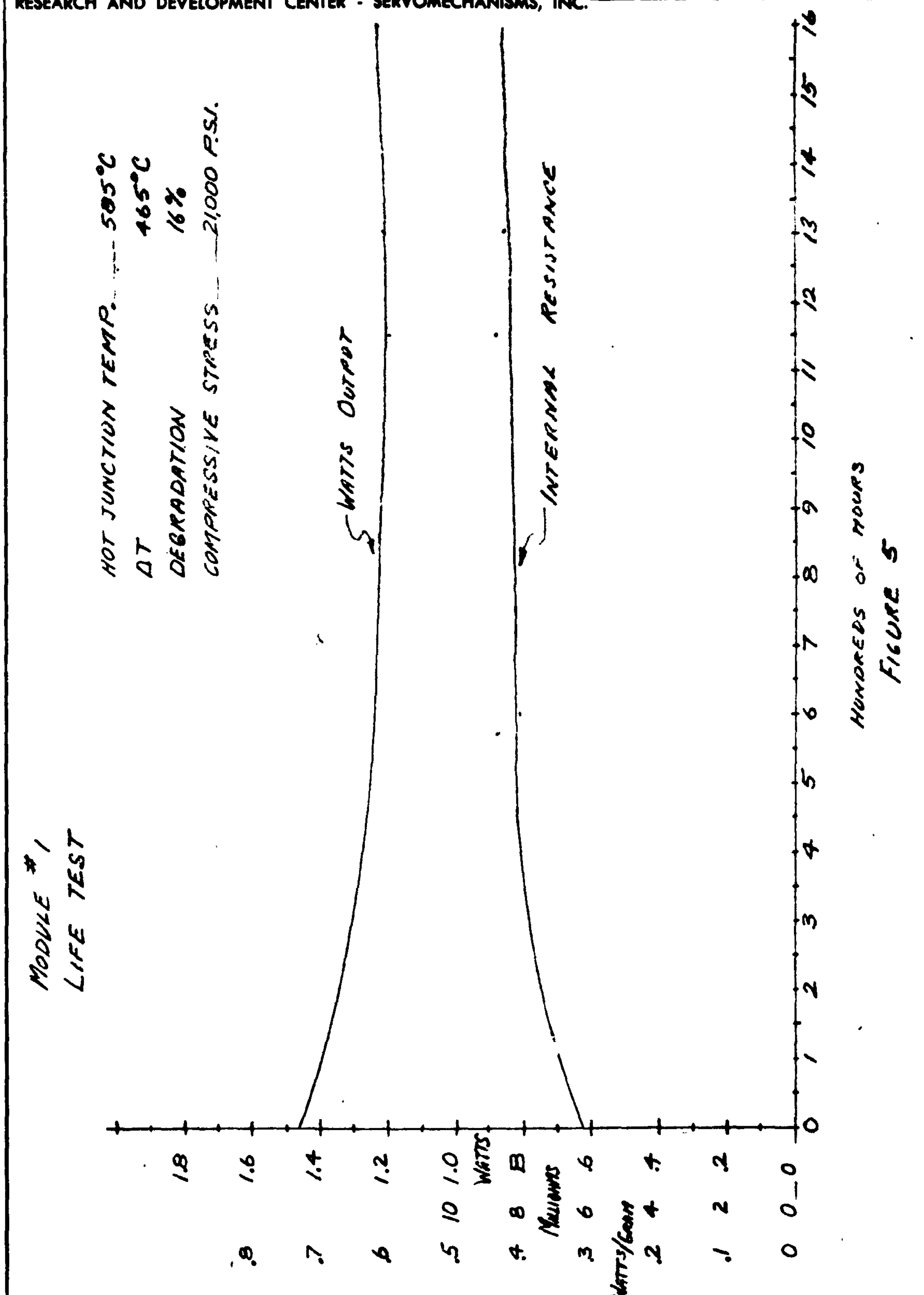

FIGURE 5

2. Test module #2 was with ARMCO iron retaining rings and mica insulators and accumulated 1,000 hours during the course of life test and showed a 12% loss of power output. The test conditions were the same as Item 1 and again, the most degradation occurred during the first 300 hours. The results are shown in Figure 6. The specific power output of this module was initially .78 watts per gram of active material.

3. Test module # 3 was also an ARMCO-mica unit and accumulated 1,000 hours during the course of the life test. The high degradation of this unit is explainable since early in its history an accidental failure of the test setup, in terms of a broken water line, caused it to operate for an unknown period of time in a steam and water vapor atmosphere. The test was continued after the correction of the failure, and the curve of Figure 7 shows a slow recovery from the artificial conditions that were imposed. Specific power was initially .69 watts per gram.

4. Test module #4 put on life test utilised ARMCO iron retaining rings and a TiO_2 insulating material. It accumulated 900 hours of life test and indicates a power output degradation of about 9%. The curve of life performance is shown in Figure 8. Specific power was initially .77 watts per gram.

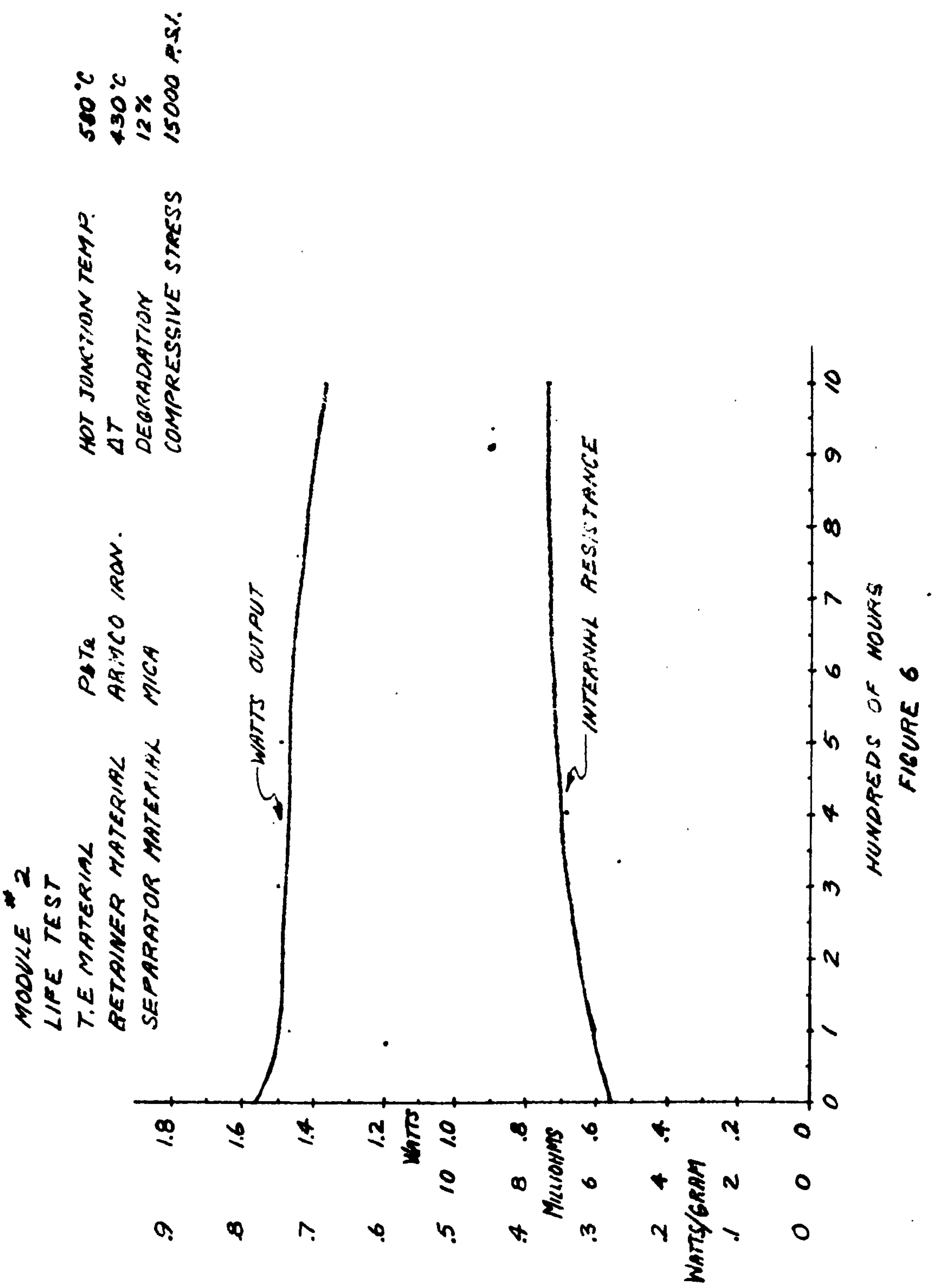
MODULE #2
LIFE TEST
T.E MATERIAL PbTe
RETAINER MATERIAL ARMCO IRON.
SEPARATOR MATERIAL MICA
HOT JUNCTION TEMP. 580°C
ΔT 430°C
DEGRADATION 12%
COMPRESSIVE STRESS 15000 P.S.I.
WATTS OUTPUT
INTERNAL RESISTANCE
WATTS
MILLIOHMS
WATTS/GRAM
HUNDREDS OF HOURS
0 1 2 3 4 5 6 7 8 9 10
1.8 1.6 1.4 1.2 1.0 .8 .6 .4 .2 0
10 8 6 4 2 0
.9 .8 .7 .6 .5 .4 .3 .2 .1 0

FIGURE 6

MODULE # 3
LIFE TEST

T.E. MATERIAL	PbTe	HOT JUNCTION TEMP.	550°C
RETAINER MATERIAL	ARMCO IRON	ΔT	400°C
SEPERATOR MATERIAL	MICA	DEGRADATION	19%
		COMPRESSIVE STRESS	17000 P.S.I.

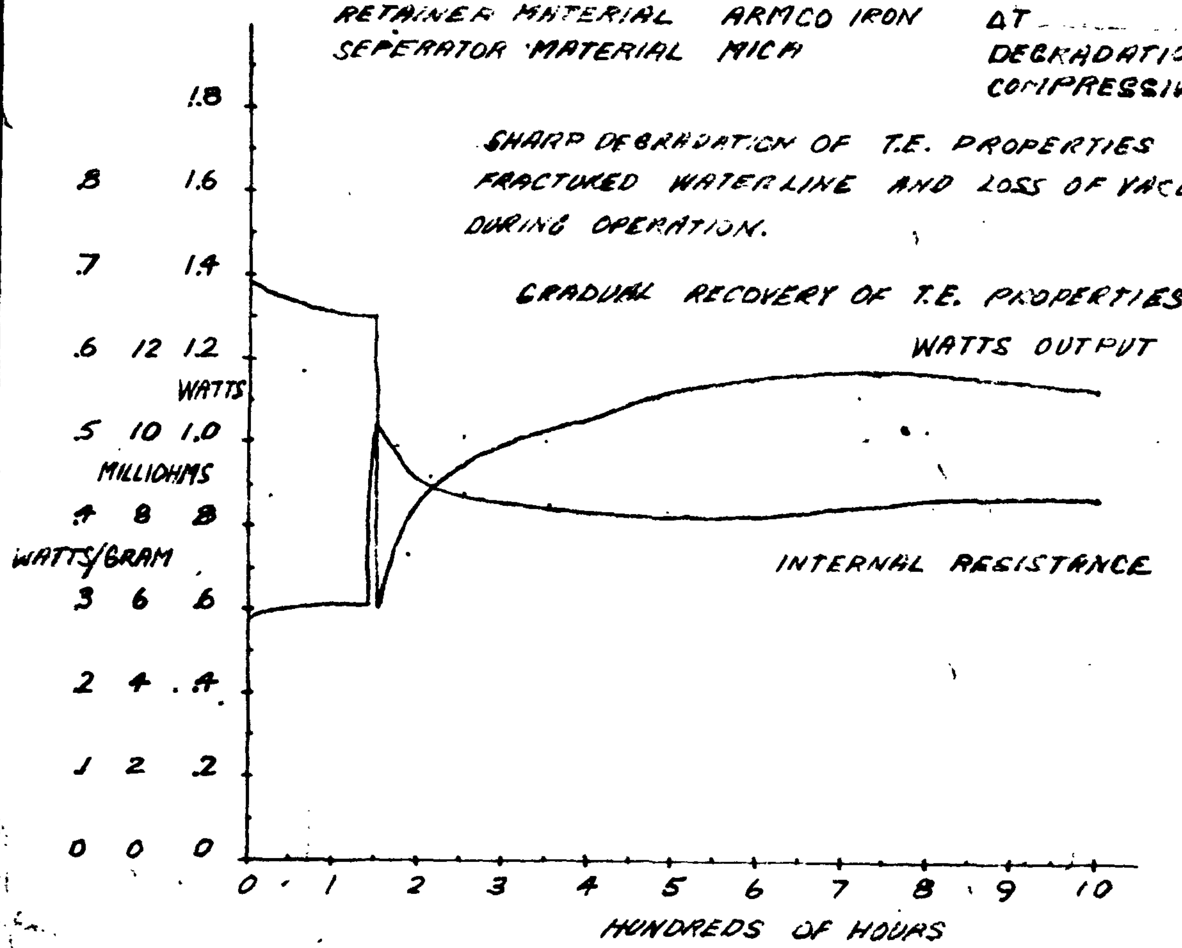

FIGURE 7

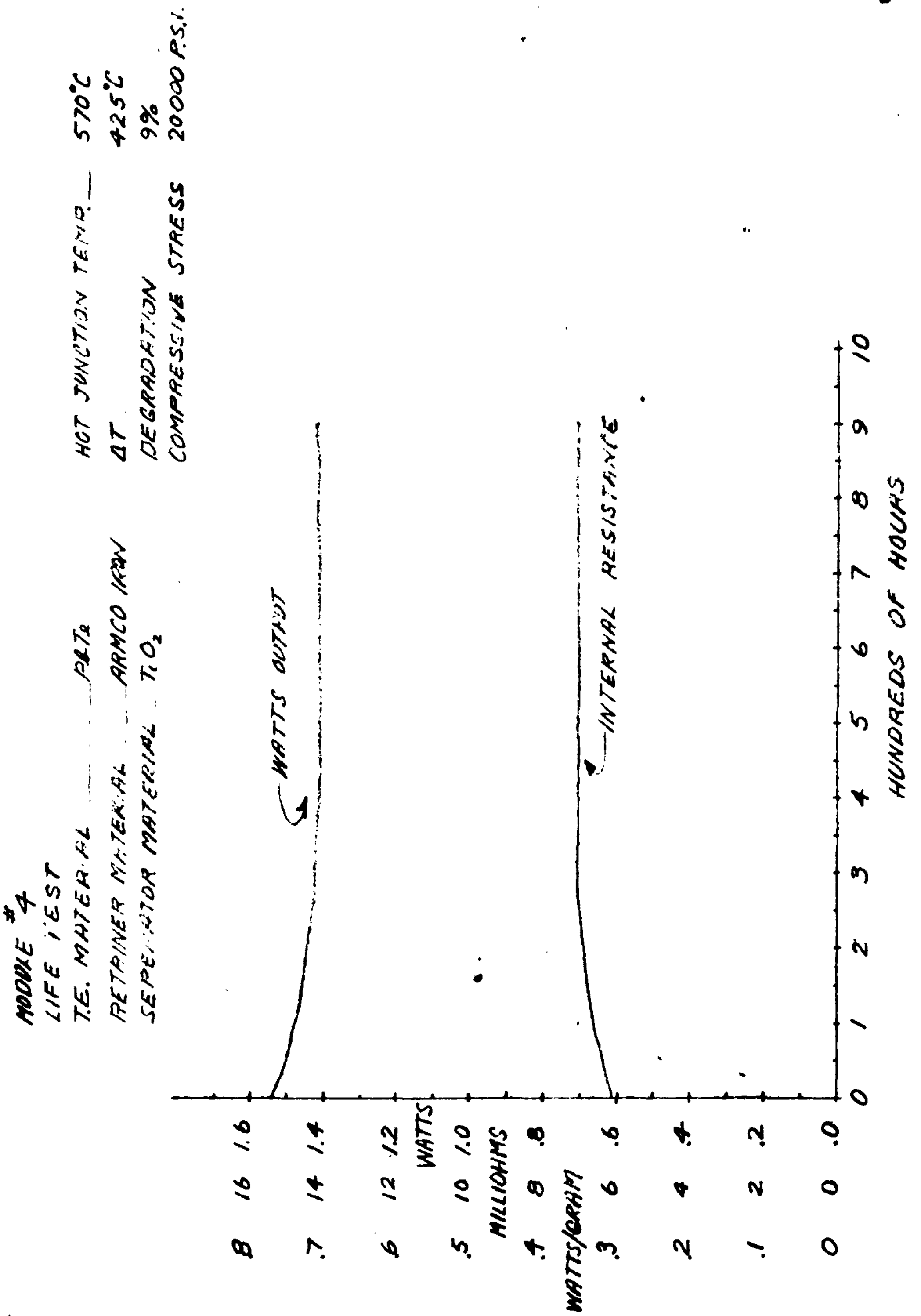
MODULE #4
LIFE TEST
T.E. MATERIAL PbTe
RETAINER MATERIAL ARMCO IRON
SEPERATOR MATERIAL TiO2
HOT JUNCTION TEMP. 570°C
ΔT 425°C
DEGRADATION 9%
COMPRESSIVE STRESS 20000 P.S.I.
WATTS OUTPUT
INTERNAL RESISTANCE
WATTS
MILLIOHMS
WATTS/GRAM
HUNDREDS OF HOURS

FIGURE 8

5. Test module #5 was constructed using AISI 416 stainless steel as the metal retaining rings and a mica wafer as the insulator. During the short period of the contract, this module experienced 330 hours of life test showing 6% of degradation, as shown in the curve in Figure 9.

6. Test module #6 was constructed utilizing AISI 430 F stainless steel for the metal retaining rings and mica as the insulating material. The short time span of the contract has only allowed 330 hours of life test on this unit which shows a 10% power degradation. This performance curve is shown in Figure 10.

B. Thermal Shock

A series of tests were carried out in order to investigate the effectiveness of compressive retainment in combating the fracturing of the thermoelectric elements caused by the thermal shock and thermal cycling. Two standard ARMCO iron contained modules which had each completed upwards of 1000 hours of continuous operation were then each subjected to 2500 thermal cycles. Figure 11 shows the temperature profile per cycle plotted as a function of time for the hot and cold junctions. Figures 12 and 13 show power output and internal resistance for each of two compressively retained modules plotted as a function

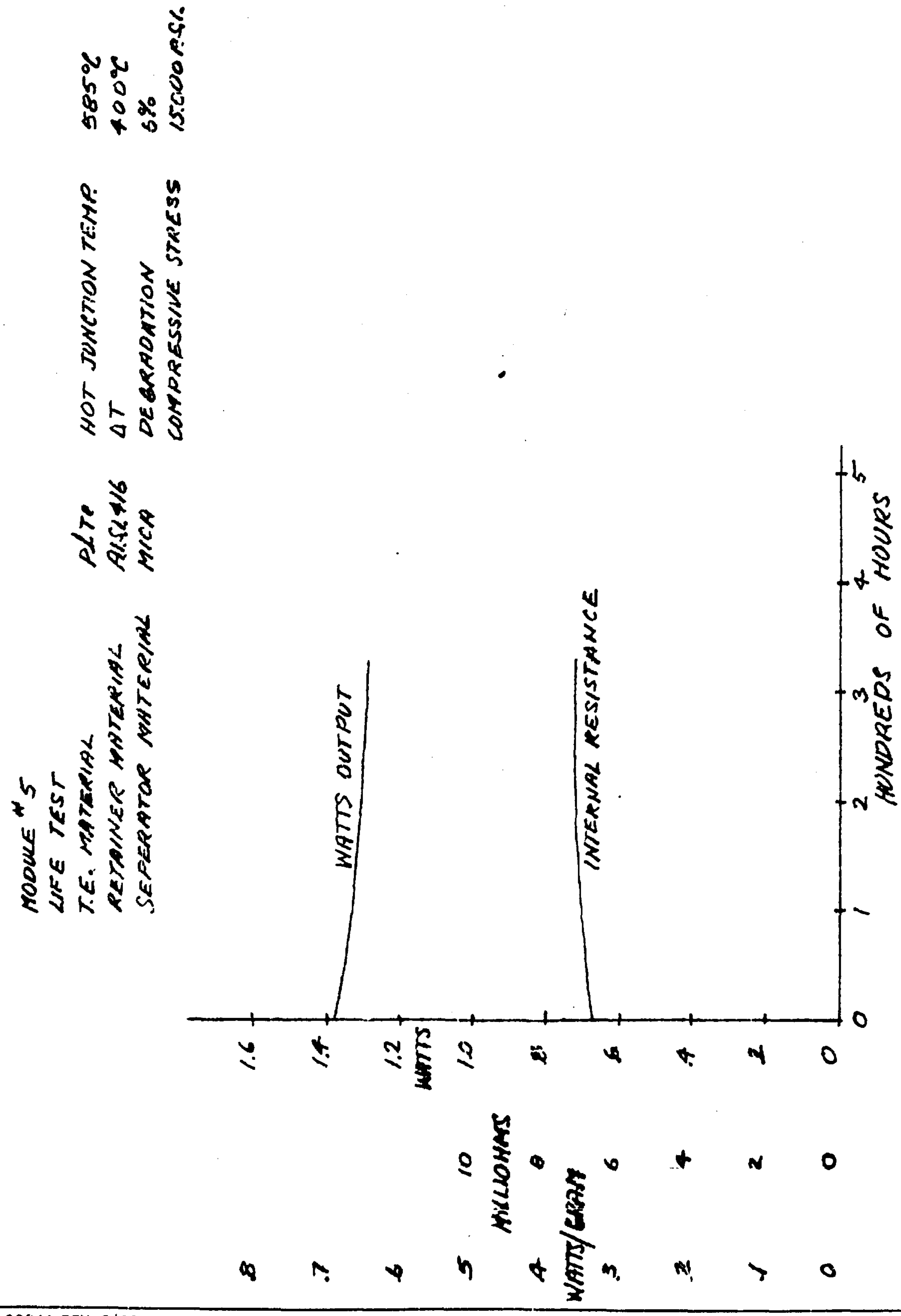
MODULE #5
LIFE TEST
T.E. MATERIAL PbTe
RETAINER MATERIAL AISI 416
SEPERATOR MATERIAL MICA
HOT JUNCTION TEMP. 585°C
ΔT 400°C
DEGRADATION 6%
COMPRESSIVE STRESS 15,000 P.S.I.
WATTS OUTPUT
INTERNAL RESISTANCE
WATTS
1.6
1.4
1.2
1.0
.8
.6
.4
.2
0
MILLIOHMS
10
8
6
4
2
0
WATTS/GRAM
.8
.7
.6
.5
.4
.3
.2
.1
0
0
1
2
3
4
5
HUNDREDS OF HOURS

FIGURE 9

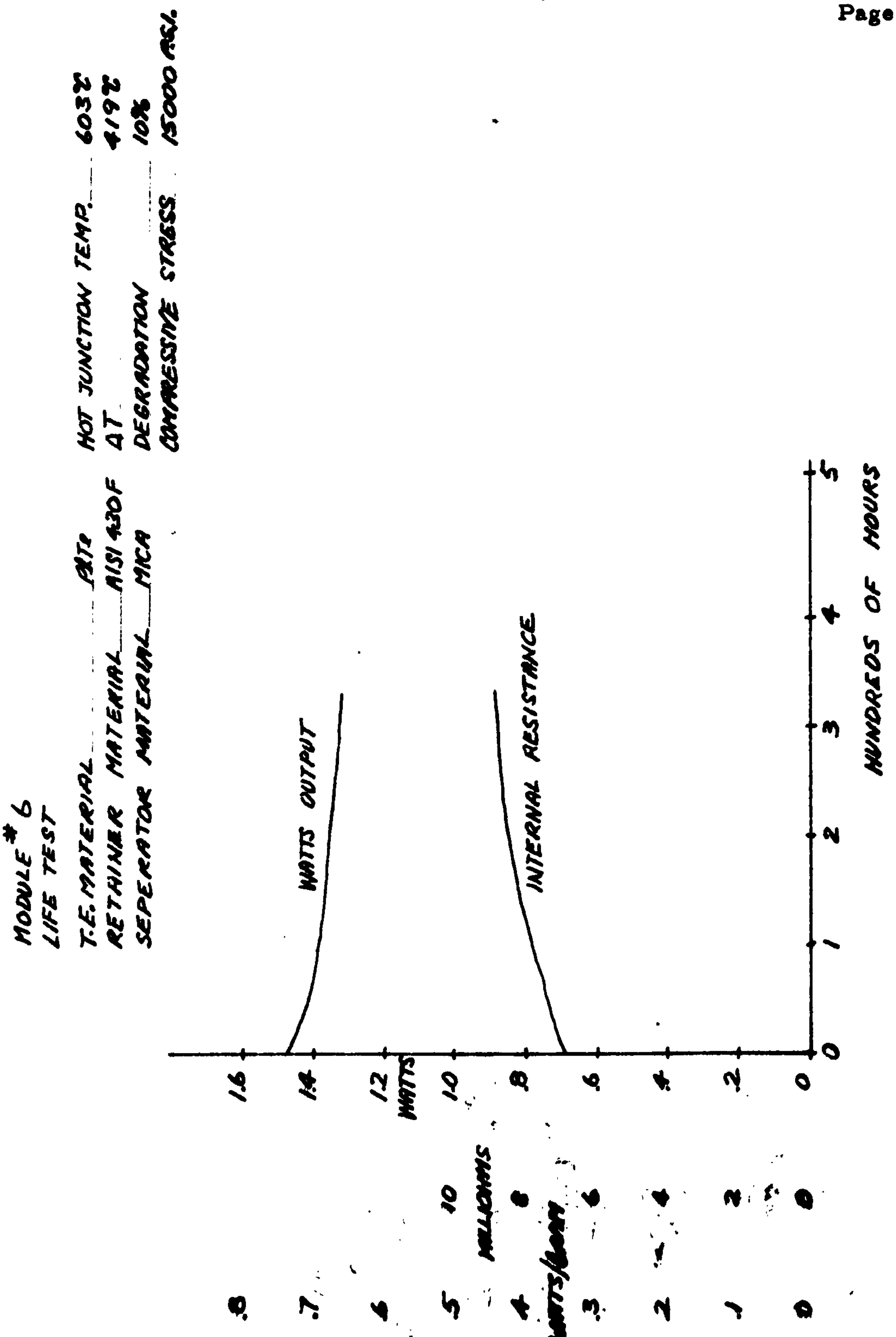
MODULE # 6
LIFE TEST
T.E. MATERIAL ____ PbTe
RETAINER MATERIAL ____ AISI 430F
SEPERATOR MATERIAL ____ MICA
HOT JUNCTION TEMP. ____ 603°C
ΔT ____ 419°C
DEGRADATION ____ 10%
COMPRESSIVE STRESS ____ 15000 PSI.
WATTS OUTPUT
INTERNAL RESISTANCE
1.6
1.4
1.2
WATTS
1.0
.8
.6
.4
.2
0
10
MILLIOHMS
8
6
4
2
0
.8
.7
.6
.5
.4
WATTS/GRAM
.3
.2
.1
0
0
1
2
3
4
5
HUNDREDS OF HOURS

FIGURE 10

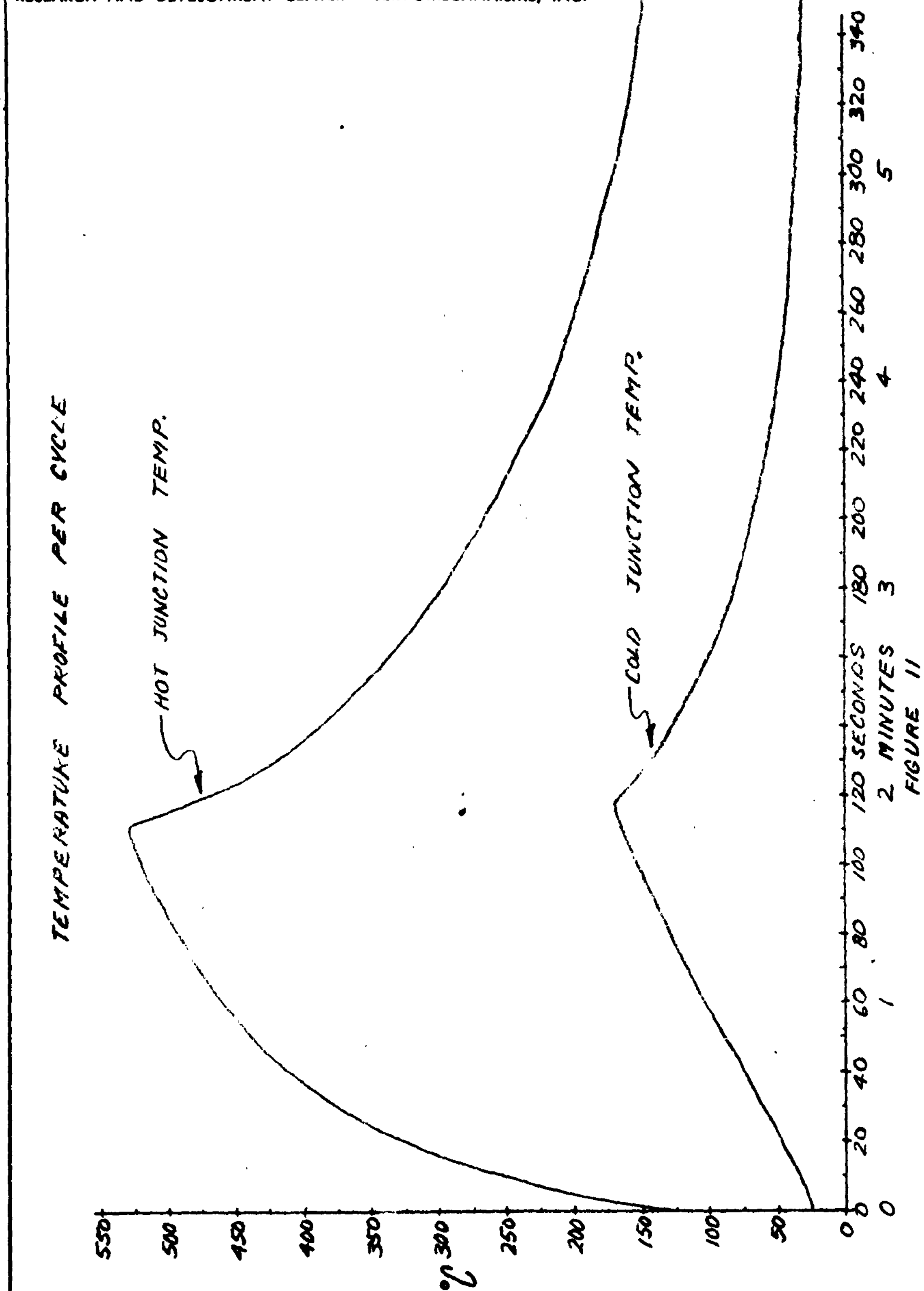
TEMPERATURE PROFILE PER CYCLE
HOT JUNCTION TEMP.
COLD JUNCTION TEMP.
°C
550
500
450
400
350
300
250
200
150
100
50
0
0
20
40
60
80
100
120 SECONDS
140
160
180
200
220
240
260
280
300
320
340
1
2 MINUTES
3
4
5

FIGURE 11

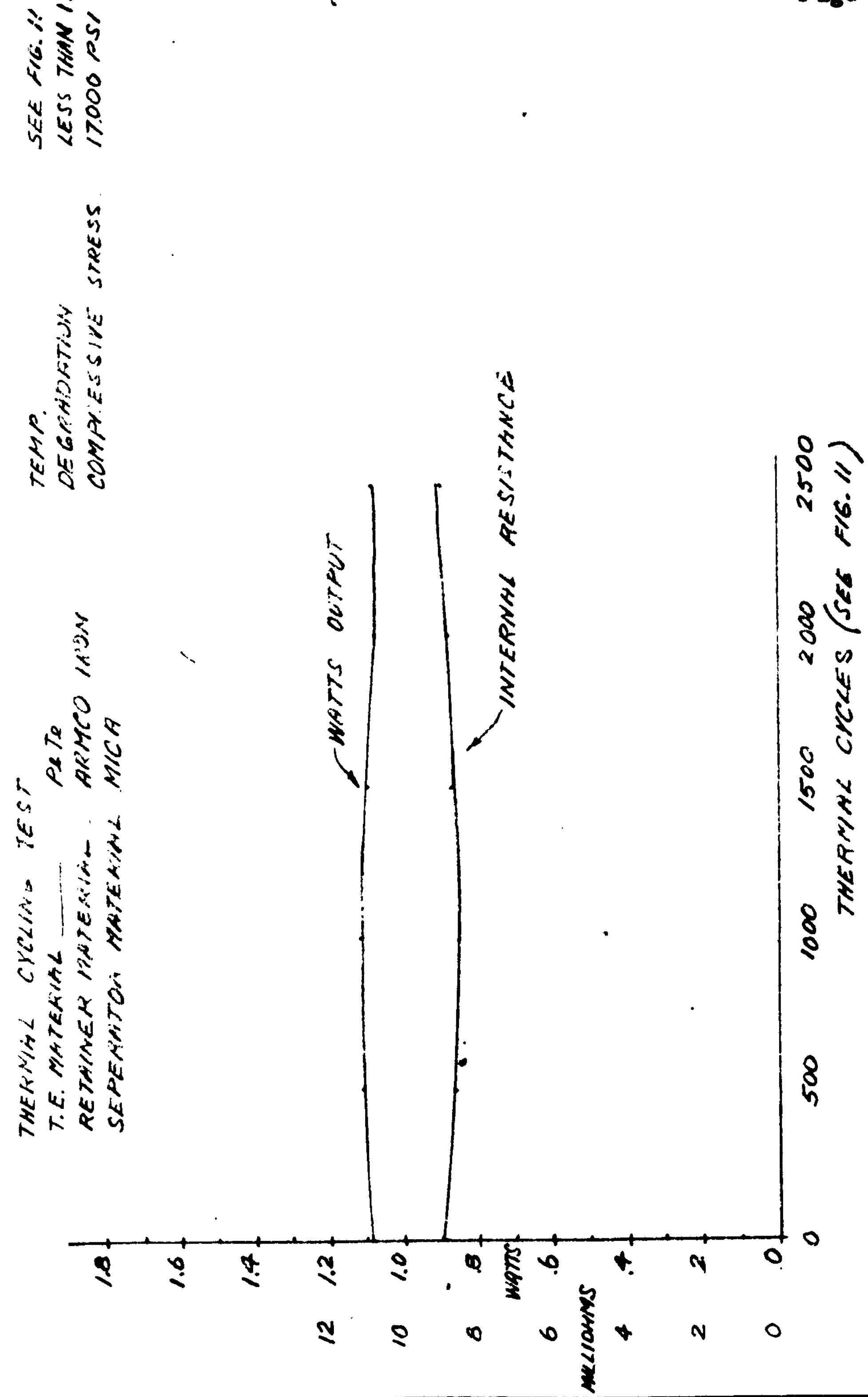
THERMAL CYCLING TEST
T.E. MATERIAL —— P_bT_e
RETAINER MATERIAL — ARMCO IRON
SEPERATOR MATERIAL MICA
TEMP. SEE FIG. 11
DEGRADATION LESS THAN 1%
COMPRESSIVE STRESS 17,000 PSI
WATTS OUTPUT
INTERNAL RESISTANCE
1.8
1.6
1.4
1.2
1.0
.8
.6
.4
.2
0
WATTS
12
10
8
6
4
2
0
MILLIOHMS
0
500
1000
1500
2000
2500
THERMAL CYCLES (SEE FIG. 11)

FIGURE 12

THERMAL CYCLING TEST			
T.E. MATERIAL	PbTe	TEMP.	SEE FIG. 11
RETAINER MATERIAL	ARMCO IRON	DEGRADATION	LESS THAN 1%
SEPERATOR MATERIAL	MICA	COMPRESSIVE STRESS	20,000 P.S.I.

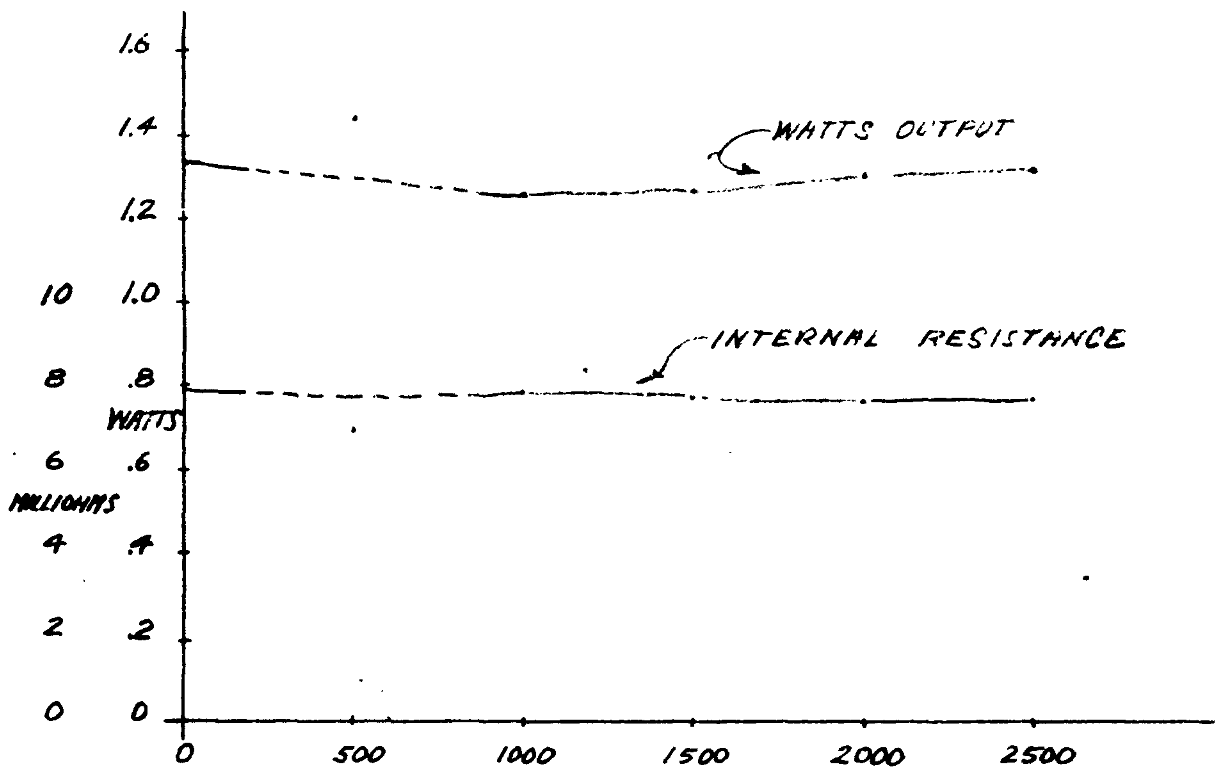

FIGURE 13

of completed thermal cycles. For comparison, Figure 14 shows a plot of the internal resistance and power output of an identical module without compressive retainment when subjected to the same thermal cycling. It is seen that the internal resistance increases quite rapidly while the Seebeck coefficient remains constant. When a condition of equilibrium was reached after approximately 360 cycles a retaining pressure of 15,000 psi was imposed and the properties of the module were observed to return rapidly to almost their original value. This series of tests indicate clearly that the compressively retained module is immune to the effects of thermal cycling and thermal shock. No tests involving mechanical shocks were carried out, but is is probable that the same immunity would be evidenced.

C. <u>Effect of Pressure on Module Thermoelectric Properties</u>

In order to determine the effect of the compressive retaining pressure upon the thermoelectric properties of a module, one of the ARMCO contained modules was placed in the test fixture in a vacuum environment and a thermal gradient imposed. The Seebeck coefficient and internal resistance were recorded while the confining pressure was varied from 32,000 psi down to 150 psi. Figure 15 summarizes the results of this test. The slight increase in Seebeck coefficient was probably a function of increasing hot junction temperature. No gross changes in

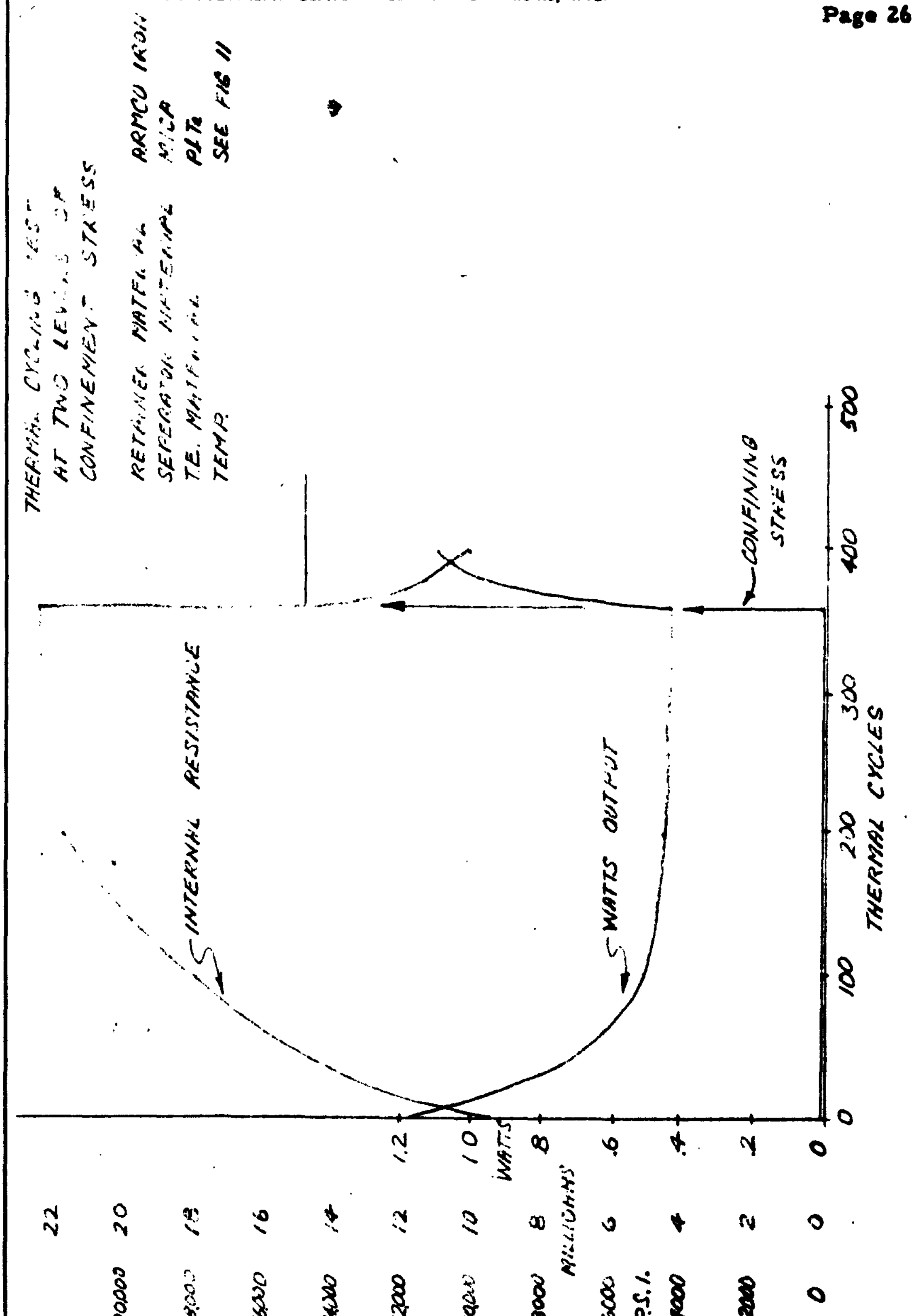
THERMAL CYCLING TEST
AT TWO LEVELS OF
CONFINEMENT STRESS
RETAINER MATERIAL ARMCO IRON
SEPERATOR MATERIAL MICA
T.E. MATERIAL PbTe
TEMP. SEE FIG 11
CONFINING STRESS
INTERNAL RESISTANCE
WATTS OUTPUT
THERMAL CYCLES
0
100
200
300
400
500
WATTS
1.2
1.0
.8
.6
.4
.2
0
MILLIOHMS
22
20
18
16
14
12
10
8
6
4
2
0
P.S.I.
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0

FIGURE 14

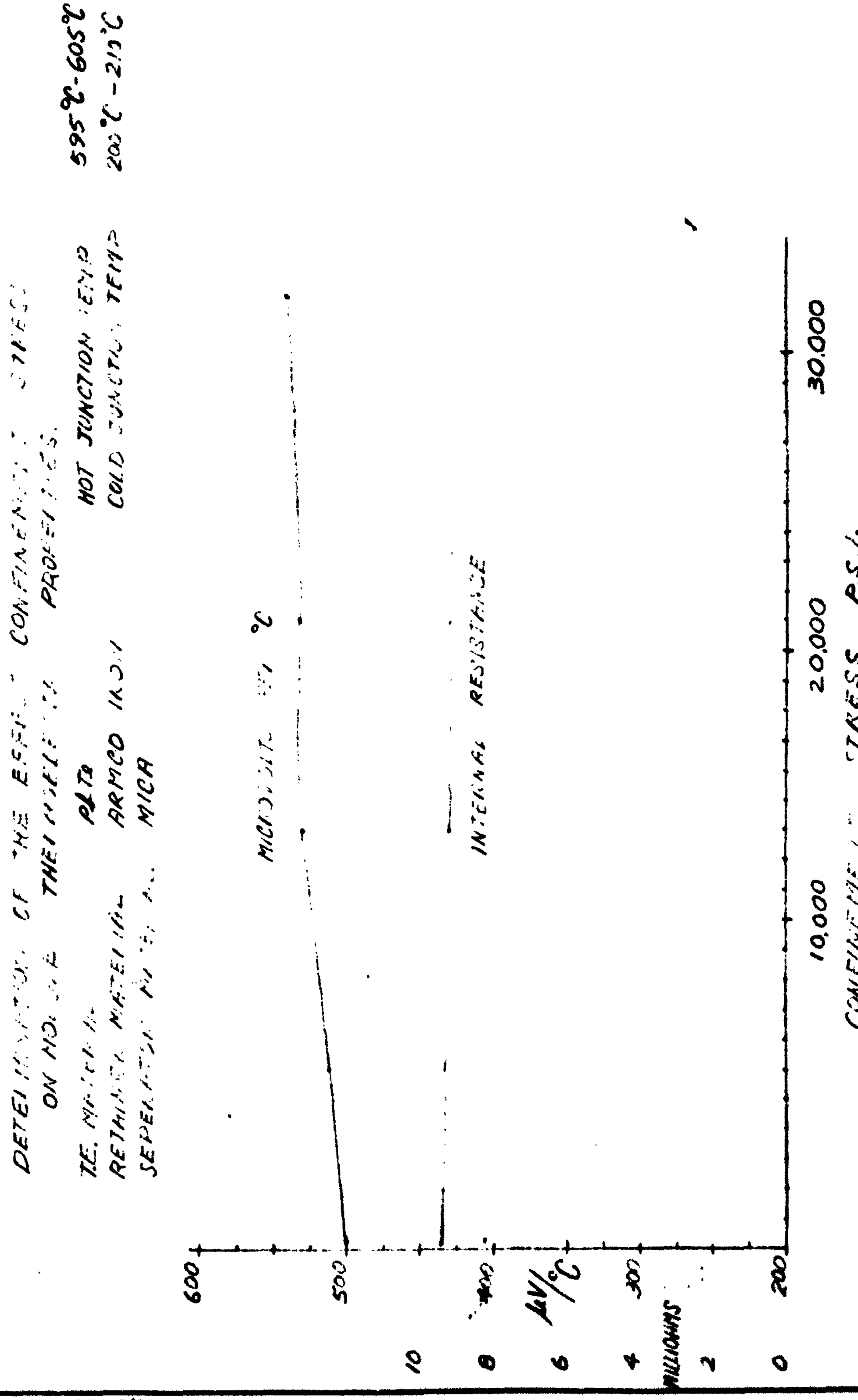
CONFINEMENT
THERMOELECTRIC PROPERTIES
HOT JUNCTION TEMP 595°C-605°C
COLD JUNCTION TEMP 200°C-210°C
PbTe
ARMCO IRON
MICA
°C
INTERNAL RESISTANCE
600
500
400
300
200
μV/°C
10
8
6
4
2
0
MILLIOHMS
10,000
20,000
30,000
STRESS P.S.I.

FIGURE 15

properties was observed to be caused by the variation of retaining pressure.

D. Materials Compatibility

Variations of the standard module were fabricated and their performance determined over a range of temperature up to 600° C. for comparison with the standard mica separated ARMCO retained module. Figures 16 through 21 summarize the results of this series of tests. For each variation of module there is a plot of module internal resistance versus temperature, Seebeck voltage versus temperature, and Seebeck voltage per degree C. versus temperature. Figure 16, for comparison, is the standard ARMCO iron retained mica separated module. Figure 17 has ARMCO retainers and ZrO_2. Figure 18 shows ARMCO iron retainers with T_iO_2 separators and Figure 19, ARMCO iron retainers with BN separators. The module whose performance is presented in Figure 20 employs AISI Type 416 stainless steel, and that of Figure 21, AISI Type 430-F stainless steel, both with mica separators. Type 416 is a martensitic stainless steel with good corrosion resistance and high temperature creep strength. AISI Type 430-F is a ferritic stainless steel exhibiting excellent corrosion resistance and high temperature creep strength. Type 430-F contains no nickel and Type 416 a small amount.

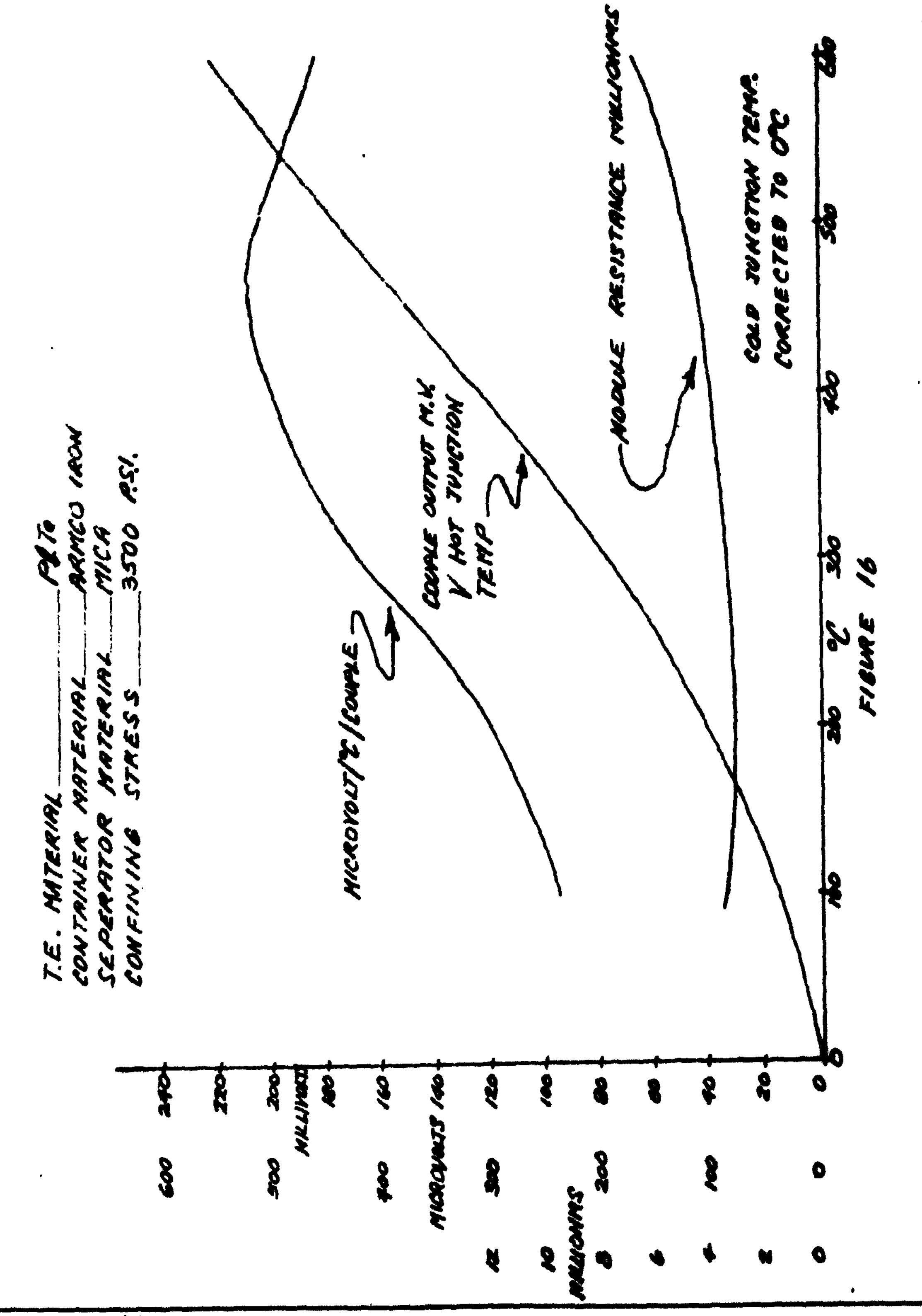
T.E. MATERIAL ______ PbTe
CONTAINER MATERIAL ______ ARMCO IRON
SEPERATOR MATERIAL ______ MICA
CONFINING STRESS ______ 3500 P.S.I.
MICROVOLT/°C/COUPLE
COUPLE OUTPUT M.V. V HOT JUNCTION TEMP
MODULE RESISTANCE MILLIOHMS
COLD JUNCTION TEMP. CORRECTED TO 0°C
°C
0 100 200 300 400 500 600
MILLIVOLTS
0 20 40 60 80 100 120 140 160 180 200 220 240
MICROVOLTS
0 100 200 300 400 500 600
MILLIOHMS
0 2 4 6 8 10 12

FIGURE 16

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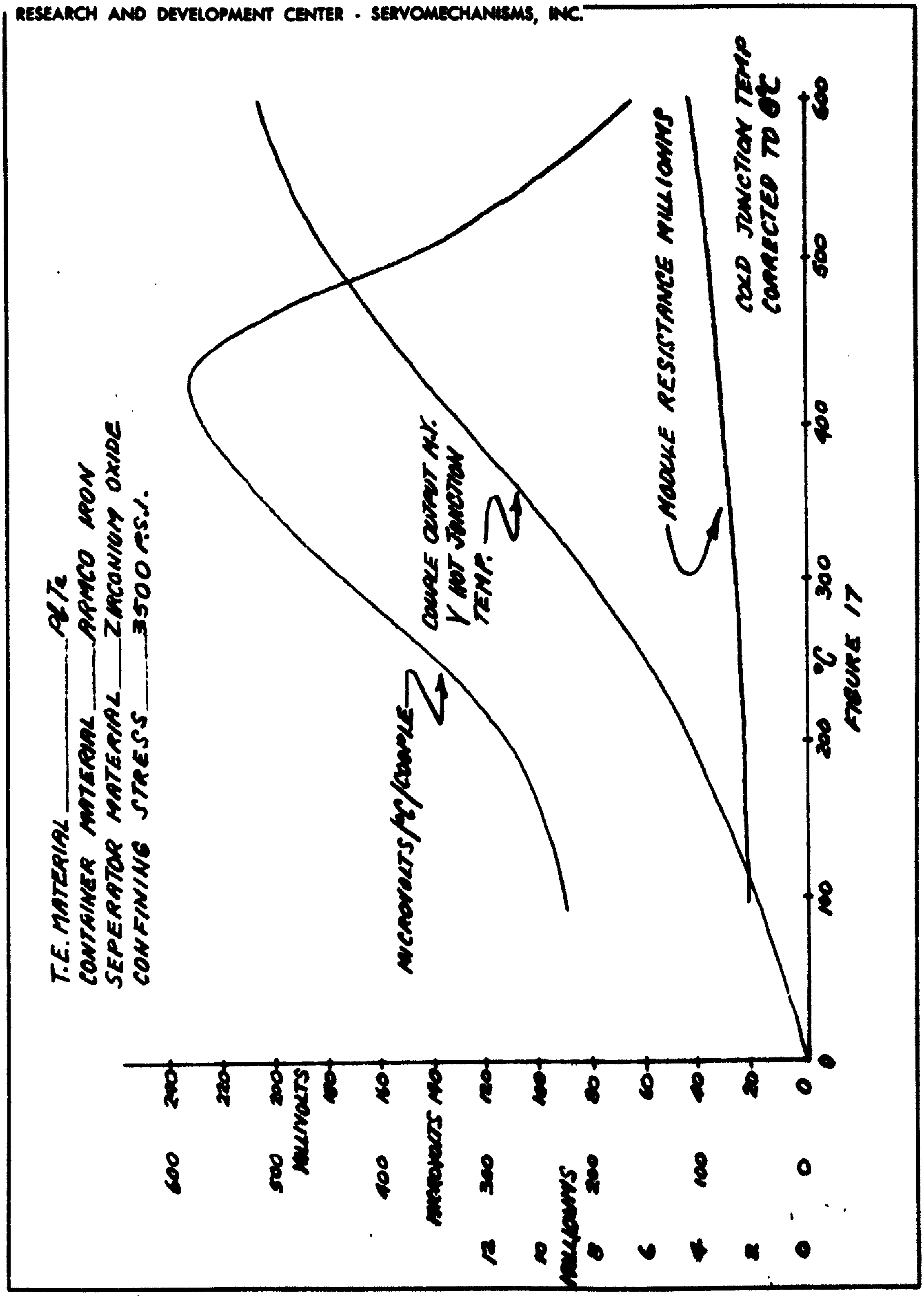

FIGURE 17

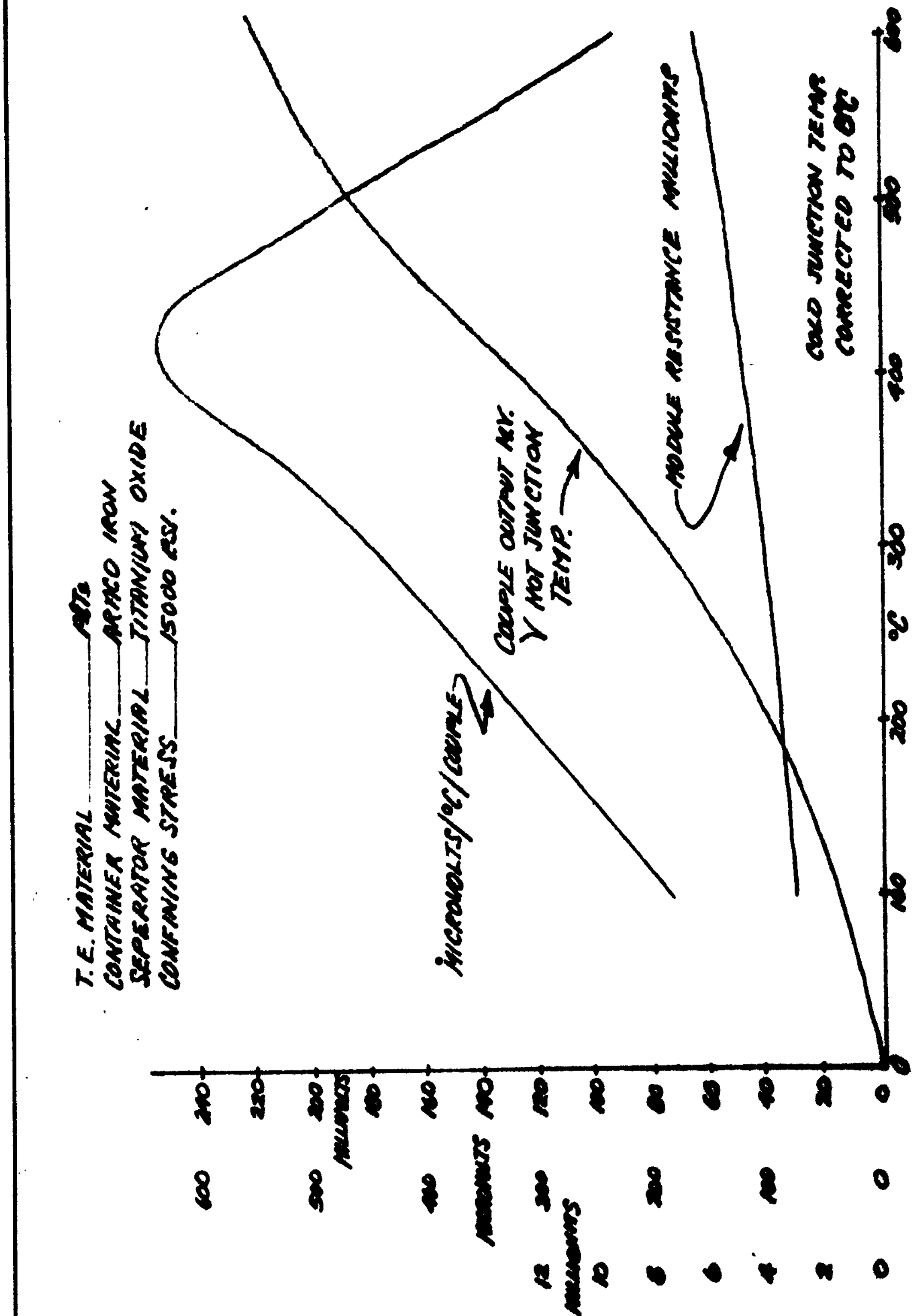
T.E. MATERIAL ____ PbTe
CONTAINER MATERIAL ____ ARMCO IRON
SEPERATOR MATERIAL ____ TITANIUM OXIDE
CONFINING STRESS ____ 15000 PSI.
MICROVOLTS/°C/COUPLE
COUPLE OUTPUT MV.
V HOT JUNCTION
TEMP.
MODULE RESISTANCE MILLIOHMS
COLD JUNCTION TEMP.
CORRECTED TO 0°C
0
100
200
300
°C
400
500
600
MILLIVOLTS
0
20
40
60
80
100
120
140
160
180
200
220
240
MICROVOLTS
0
100
200
300
400
500
600
MILLIOHMS
0
2
4
6
8
10
12

FIGURE 18

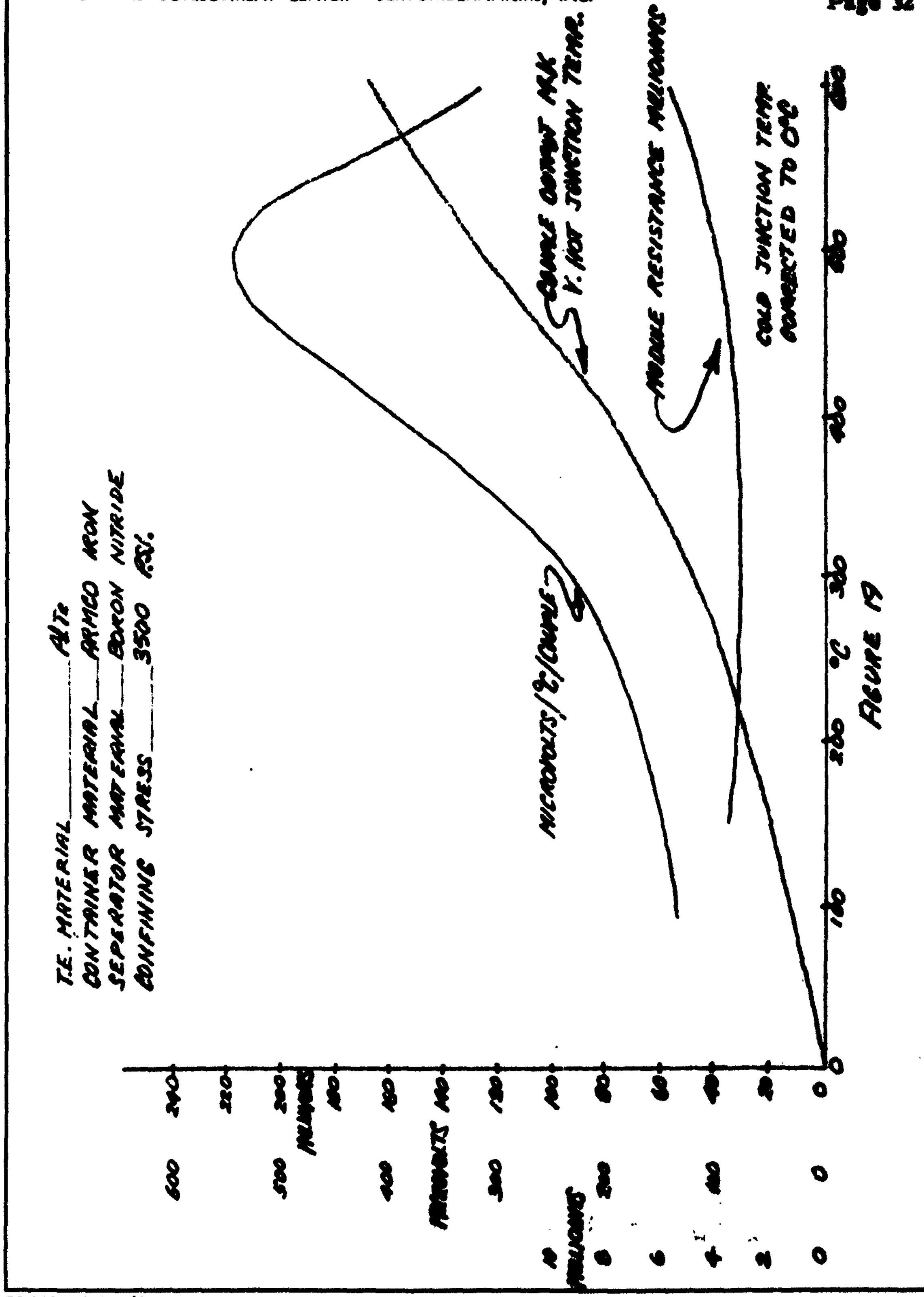
T.E. MATERIAL AlTe
CONTAINER MATERIAL ARMCO IRON
SEPERATOR MATERIAL BORON NITRIDE
CONFINING STRESS 3500 PSI.
COUPLE OUTPUT MV. V. HOT JUNCTION TEMP.
MODULE RESISTANCE MILLIOHMS
COLD JUNCTION TEMP. CORRECTED TO 0°C
MICROVOLTS/°C/COUPLE
0
100
200
300
400
500
600
°C
MICROVOLTS
MILLIVOLTS
MILLIOHMS

FIGURE 19

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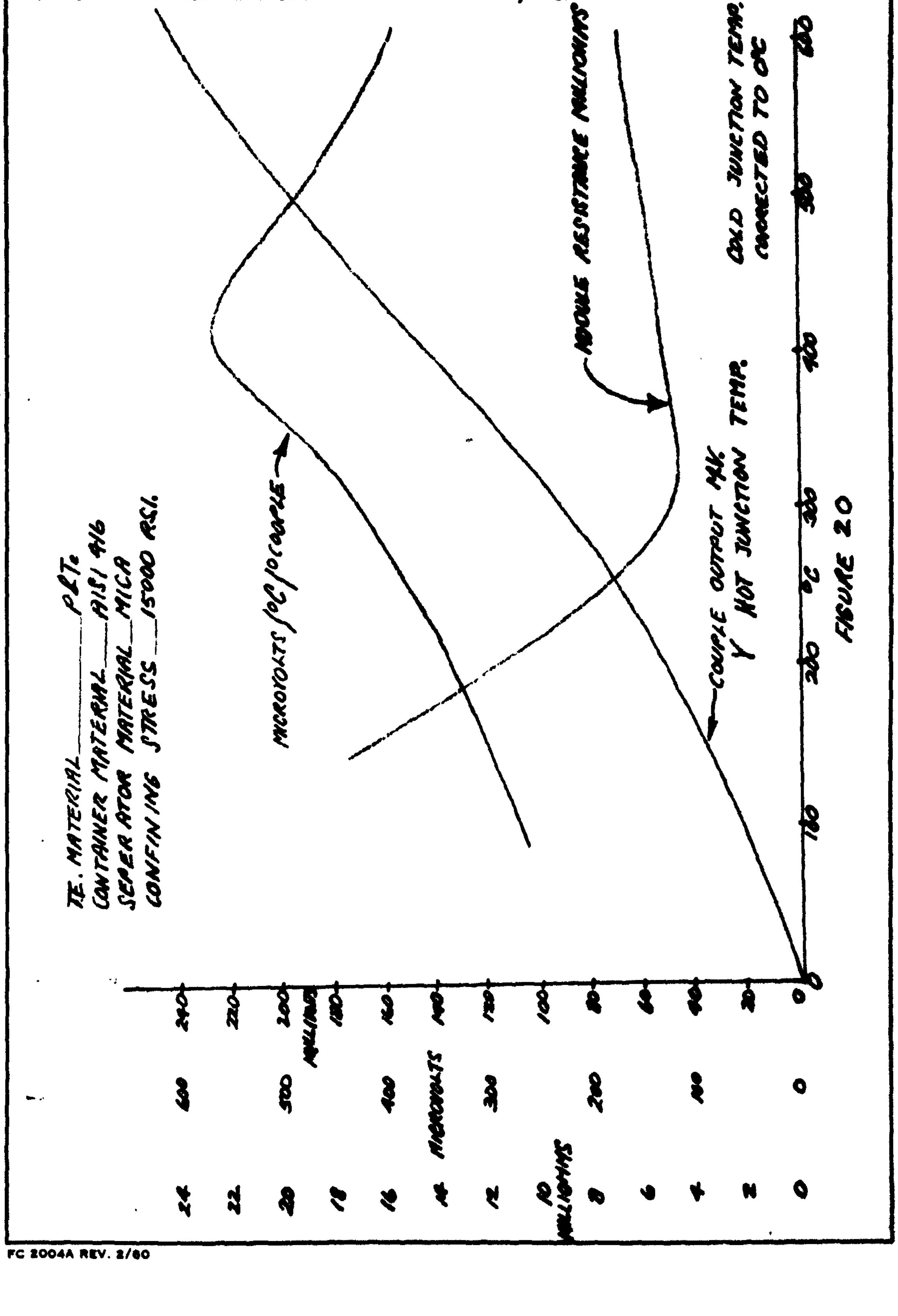


FIGURE 20

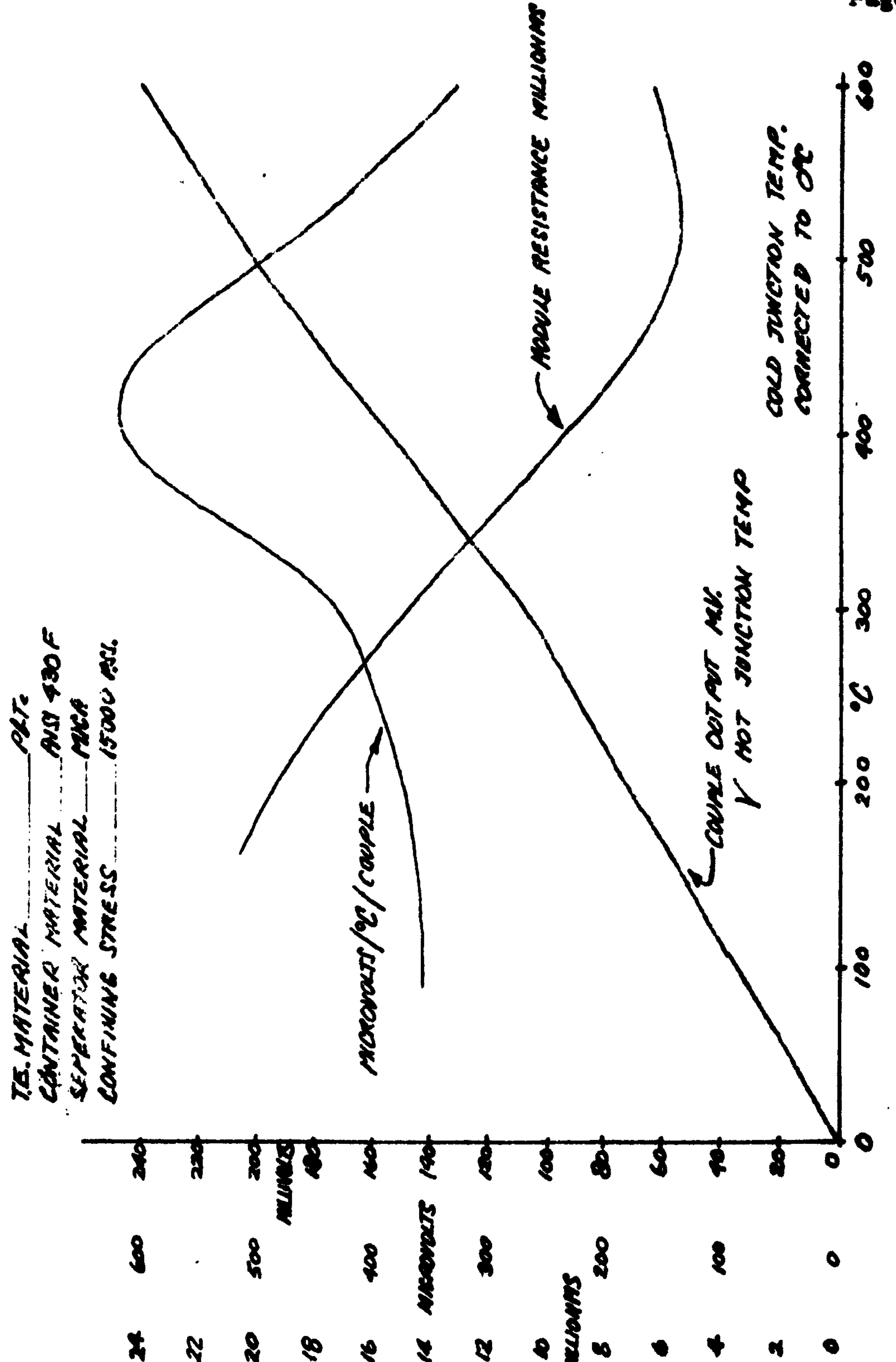

T.E. MATERIAL ____ PbTe
CONTAINER MATERIAL ____ AISI 430 F
SEPERATOR MATERIAL ____ MICA
CONFINING STRESS ____ 15000 PSI.
MODULE RESISTANCE MILLIOHMS
MICROVOLTS/°C/COUPLE
COUPLE OUTPUT MV.
V HOT JUNCTION TEMP
COLD JUNCTION TEMP.
CORRECTED TO 0°C
0
100
200
300
°C
400
500
600
MILLIVOLTS
MICROVOLTS
MILLIOHMS

FIGURE 21

CHEMICAL ANALYSIS

Sample	C	Mn	P	Su	Si	Cr	Ni	Mo	Cu
416	.10	.42	.015	.330	.60	13.19	.18	.05	.09
430-F	.06	.48	.012	.254	.38	17.61		.33	

PHYSICAL PROPERTIES

Sample	Yield Strength in Pounds per Square Inch	Tensil Strength in Pounds per Square Inch	Elongation in Percentage Inch per Inch	Reduction of Area Percentage
416	75,000	98,000	21.5	58.9
430-F	80,600	93,000	28	60.4

These modules were assembled and heat treated as described under module fabrication. It is suggested that these results be taken as an indication of probable behavior since individual modules rather than a series of identical modules provided the data for each representative plot.

E. Effect of Heat and Pressure During a Sintering and Heat Treatment Fabrication Process

The individual modules must be heat treated after the cold swaging process and before evaluation in order to develop acceptable internal resistance. Figure 22 summarises the results of the approximate optimization of the heat treatment of the standard ARMCO iron contained

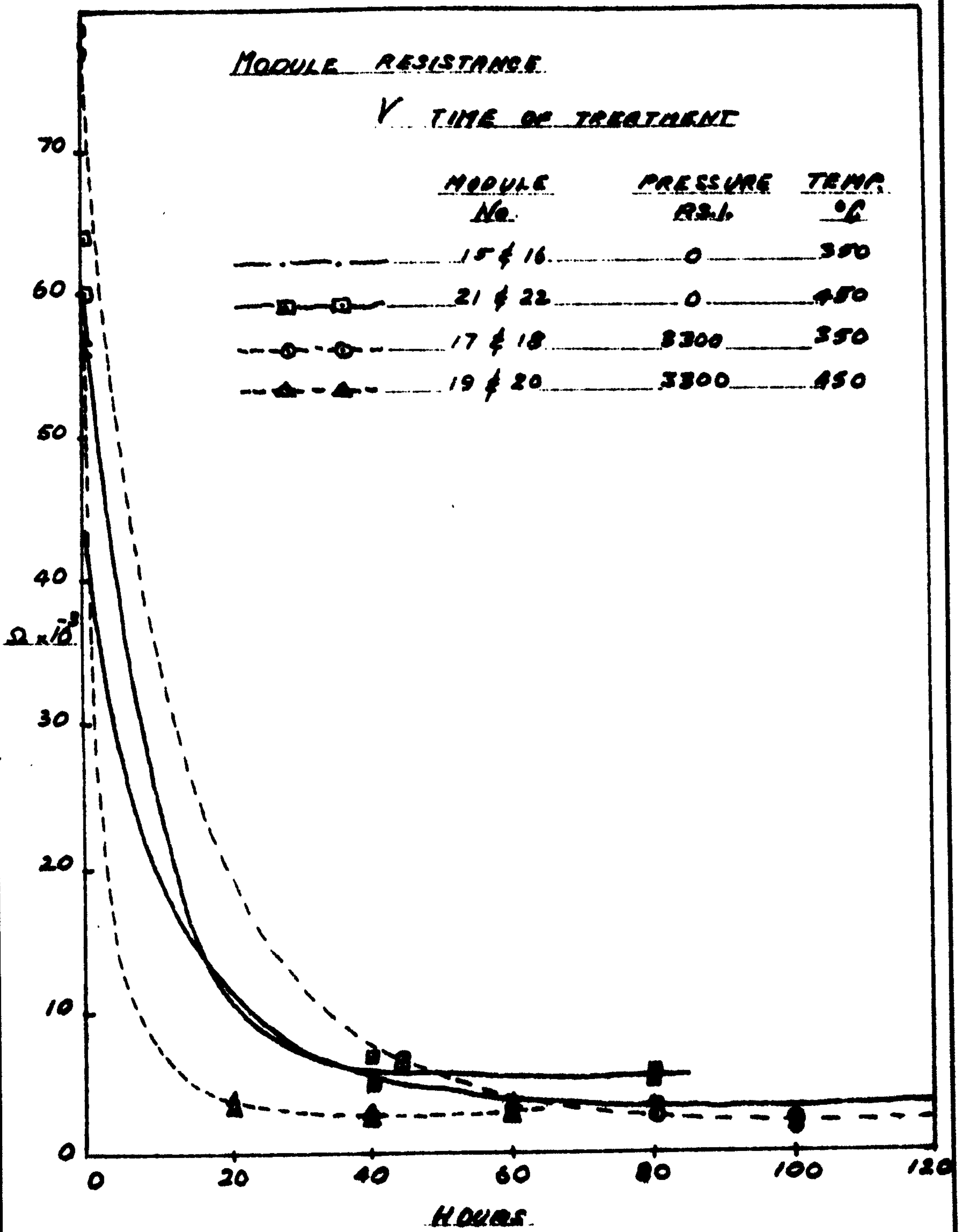

MODULE RESISTANCE
V. TIME OF TREATMENT
MODULE No.
PRESSURE P.S.I.
TEMP. °C
15 & 16 0 350
21 & 22 0 450
17 & 18 3300 350
19 & 20 3300 450
70
60
50
40
$\Omega \times 10^{-3}$
30
20
10
0
0
20
40
60
80
100
120
HOURS

FIGURE 22

module. The electrical resistance of the modular couple assembly including the hot and cold junction contacts is plotted as a function of time for various selected temperatures and pressures of heat treatment. From a consideration of the geometry of the module, it can be shown that a module resistance of $10^{-3}\,\Omega$ corresponds to a mean resistivity of $1.17 \times 10^{-3}\,\Omega$ cm. It does not seem therefore, that the junction contacts are contributing significantly to the internal resistance of the modules. It is evident that the rate of development of these properties is accelerated by both the application of temperature and pressure; further, that this effect is more influenced by temperature. If the heat treatments were carried out in a good vacuum, the results would have been more satisfactory. The pressure level of 3500 psi was chosen for heat treatment since it had been previously determined that this was above the yield strength of the lead telluride at the heat treatment temperature. Appendix B discusses the variation of compressive yield strength of lead telluride with temperature.

V. CONCLUSION

The conclusion to be derived from the examination of the test data in the previous section indicates that the technique of the pressure containment of the semiconductive material does give significant advantages. Although some degradation was indicated in the life tests, the test conditions were unusually severe and, without the pressure containment technique, the unit most probably would not have survived. It indicates that prolonged operation at 600° C. in vacuum environment is possible with this technique with relatively low degradation, most of which occurs in the first 300 hours of operation. During life test operation of the units, there was no evidence in the test container of loss of tellurium due to sublimation, which certainly would have been very pronounced at these temperatures without the pressure containment technique.

The thermal shock testing indicates that units built by this method are totally immune to start-up - shut-down cycling. This is a severe test, and most other methods of construction show severe degradation due to the formation of cracks.

It has also been proven that the use of thermoelectric material under conditions above its compressive yield strength does not have significant effect on its thermoelectric behavior. The tests with

various structural materials indicate no serious problems with retaining rings or with the insulation.

Although the test program was conducted with fairly small thermoelectric elements as individual couples, the techniques could be applied to full scale thermoelectric generators. The individual modules can be stacked to form a series of couples, as shown in Figure 23. This method of construction offers the advantage of being able to fabricate individual couples and thoroughly test them before assembly into a complete thermoelectric generator. The size of the test modules was relatively small and was selected arbitrarily purely for test purposes. In actual application, the size of the individual modules could be increased several times to give greater power output per module and to allow more flexibility in the heat input sources.

The tests indicate that generators utilizing this principle can be operated with high thermal gradients, which may be used to give high specific output, since the use of high thermal gradients would lead to high thermal flux densities. In thermoelectric generators, the power output is proportional to the thermal flux density, and the efficiency is not affected, so that higher output per gram of thermoelectric material is obtained. Specific outputs approaching one watt per gram of thermoelectric material were obtained with good life

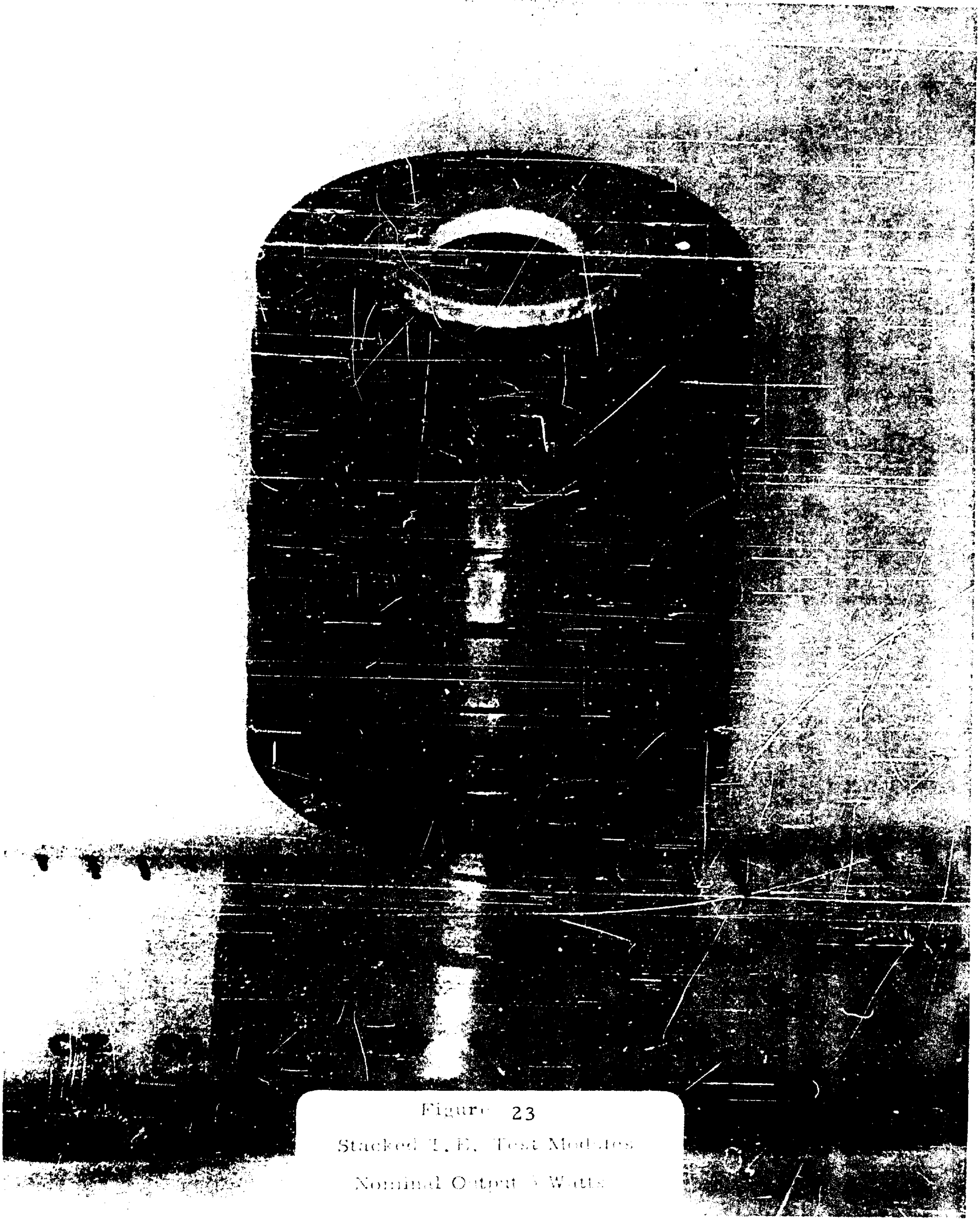


Figure 23

Stacked T.E. Test Modules

Nominal Output 5 Watts

expectancy. It is felt that in operating at these conditions, two watts per gram would be readily obtainable. The thermal flux density at the hot junction will be in the order of 400 watts per square inch. To harness this approach with emphasis on high specific power output requires a heat source capable of supplying the required thermal flux density. One possible application is the use of an atomic reactor heat source in which the hot junction input could be supplied with a liquid metal transfer loop from the reactor. In this approach, a substance such as NaK could be piped through this cylindrical hot junction and adequate thermal flux could be obtained.

It would generally be difficult to obtain this high value of thermal flux density directly from flame sources of heat, even with the introduction of turbulent flow. Thermal densities between 50 and 100 watts per square inch are probably the maximum obtainable directly from flame sources. However, it has been shown that radiant heating is an interesting method of power transfer at the temperatures involved. Therefore, it is felt that a radiating solid body operating at considerably higher temperature than the desired 600°C. of the hot junction could supply the thermal flux densities required for high specific output. A burner which is suitable for this type application has been developed by Consolidated Diesel Electric Corporation in Bethel, Connecticut, and there may be other such burners.

This is a re-entrant type burner containing a small silicon carbide cylinder which can be operated at temperatures up to 1,700°C. using either gas or liquid fuels. Radiant heat transfer from such a burner could probably supply the thermal flux densities.

The thermoelectric generator construction technique described herein would also be applicable to uses where high specific power output is not important and more normal hot junction temperatures are used. Normal flame sources could be used for hot junction temperatures up to 450° C. and the benefits of this construction would lie in reliable long life with very high resistance to mechanical and thermal shocks and rapid response to turn-up and turn-down commands.

MATERIAL PREPARATION

Two identical samples of each type of lead telluride were used in the test program. These samples were in the form of discs one-half inch in diameter and one-eighth inch thick. The cast material was crushed, passed through 100 mesh and cold pressed at 30,000 psi. The resulting biscuits were then sealed in a quartz tube under vacuum and initially heat treated at 700° F., then cooled 50° F per day, to 300° F. No metallographic examinations were made of these samples. The heat treated samples were then each placed alternately in the separate apparatuses for the measurement of electrical and thermal conductivity.

The temperature of these tests was limited to 350°C. because of evaporation problems commonly encountered with unencapsulated lead telluride above these temperatures. Of the two samples of each type of lead telluride, each was alternately placed on the apparatus for electrical conductivity measurement and then that for thermal conductivity and Seebeck coefficient determination.

Electrical conducitity was measured by a four-point probe with microscopic penetration of the surface. The apparatus provided a vacuum environment and was equipped with heater, muffle, and radiation shields in order to produce a uniform sample temperature.

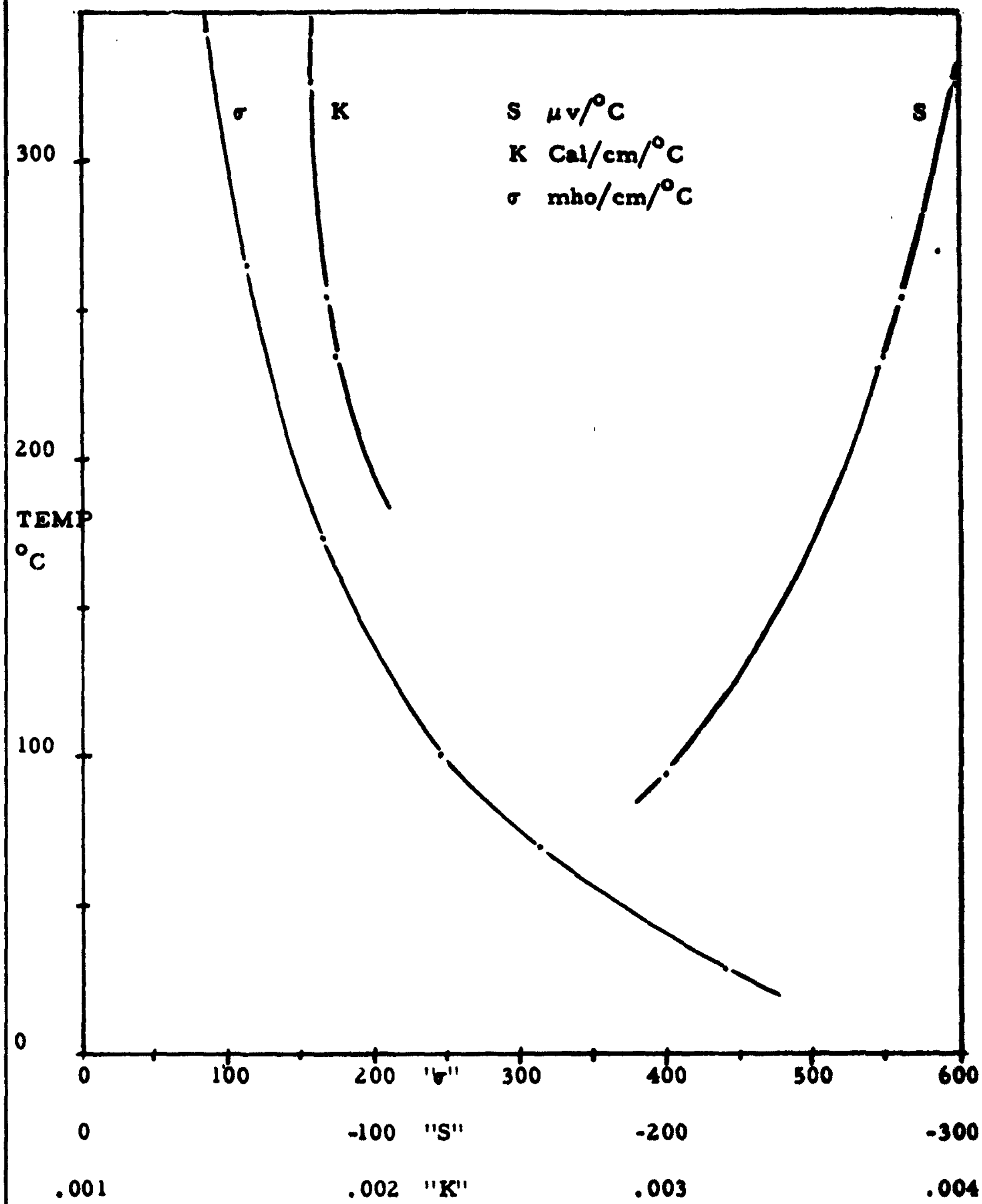
In order to measure thermal conductivity, the sample was sandwiched between two precise half-inch-diameter discs of alumina. Logi-

tudinal heat flow through the stack was induced by means of a heater placed at one end and a heat sink at the other end. The whole was surrounded by a muffle, furnace elements and radiation shields, and maintained in a vacuum. Considerable care was taken in the design of this apparatus to encourage unidirectional heat flow from the heat source to the heat sink; however, the method of computation took into account radial heat losses from the sample. Computations were based on the measured absolute temperatures occurring at each face of the two alumina standards and the sandwiched lead telluride sample. Some difficulties which were encountered concerning thermocouple calibration and radial heat losses were overcome and acceptable results were eventually obtained. The Seebeck voltage developed as a result of the temperature gradient which was maintained in order to measure thermal conductivity conveniently enable Seebeck measurements to be made at the same time. Some data which was obtained from these runs is presented in Figures 1 through 4.

The thermoelectric materials used in this work are basically lead telluride of the alloyed type. The "N" material contains 18 $\underline{M}$ % lead selenide to reduce the thermal conductivity. This alloy was doped with bromine as lead bromide to yield .05 $\underline{M}$ %. An excess of .5 $\underline{M}$ % lead is added to aid the electrical conductivity across the inter-crystalline boundaries and improve the doping yield. The doping is achieved from a dope concentrate of lead bromide and lead dissolved in tellurium.

The initial doping yielded carrier concentration about 60 % of the bromine ion concentration and it was necessary to add additional lead bromide to compensate. This yield is effected by the crystallization conditions. The redoping yielded an "N" type lead telluride with a factor having a maximum "Z" of about $1.1 \times 10^{-3}/°C$ at 200° C.

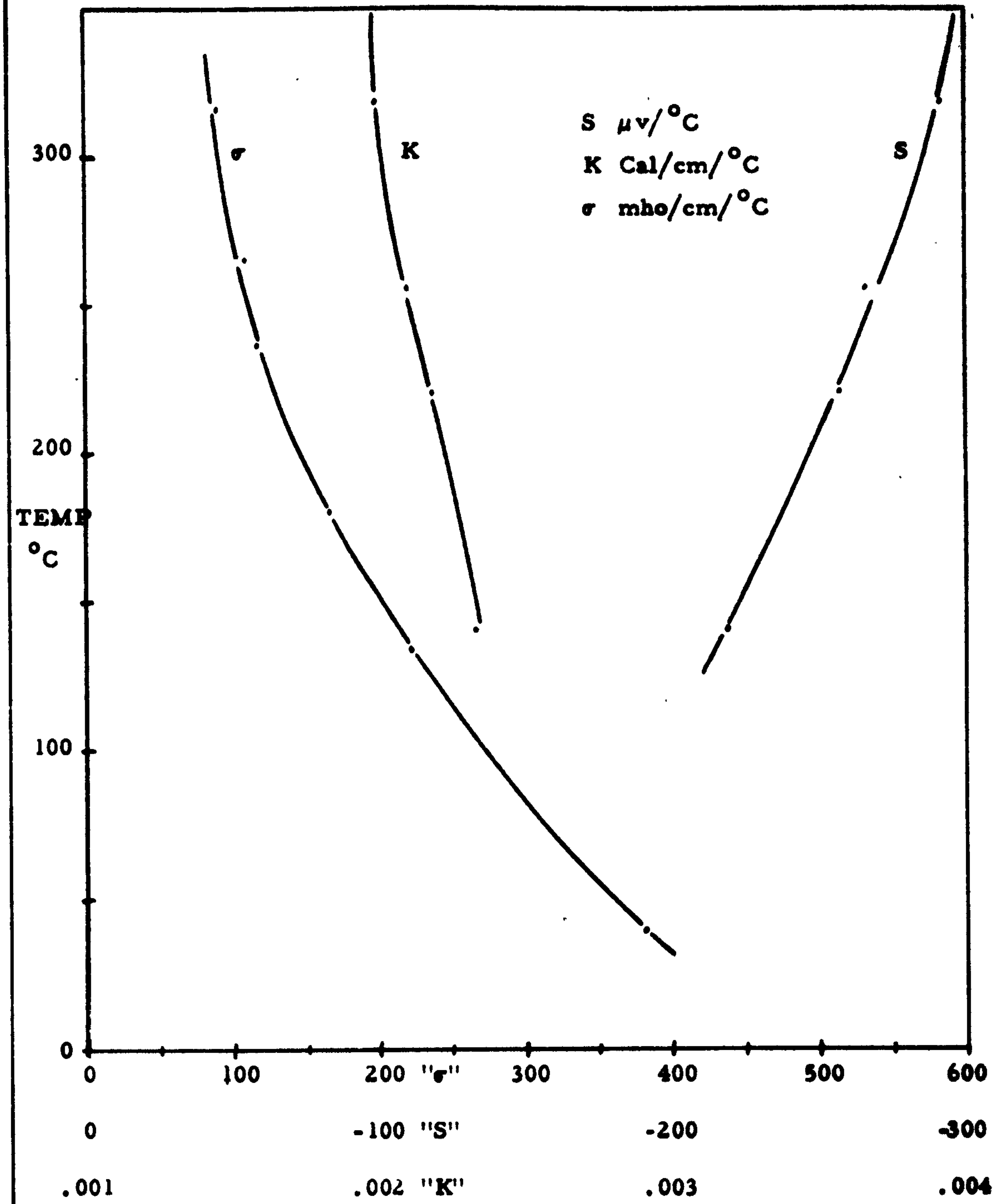
The "P" type lead telluride was likewise of the alloyed type containing 18 M % tin telluride. The doping was Sodium added from a lead-sodium alloy and the resulting material contained .6 M % sodium and .2 M % excess tellurium. The resulting material yielded a higher carrier concentration than was expected with the consequence that the Seebeck voltage was low and the "Z" factor about $.4 - .6 \times 10^{-3}/°C$.



Lead Telluride N Type Sample #1

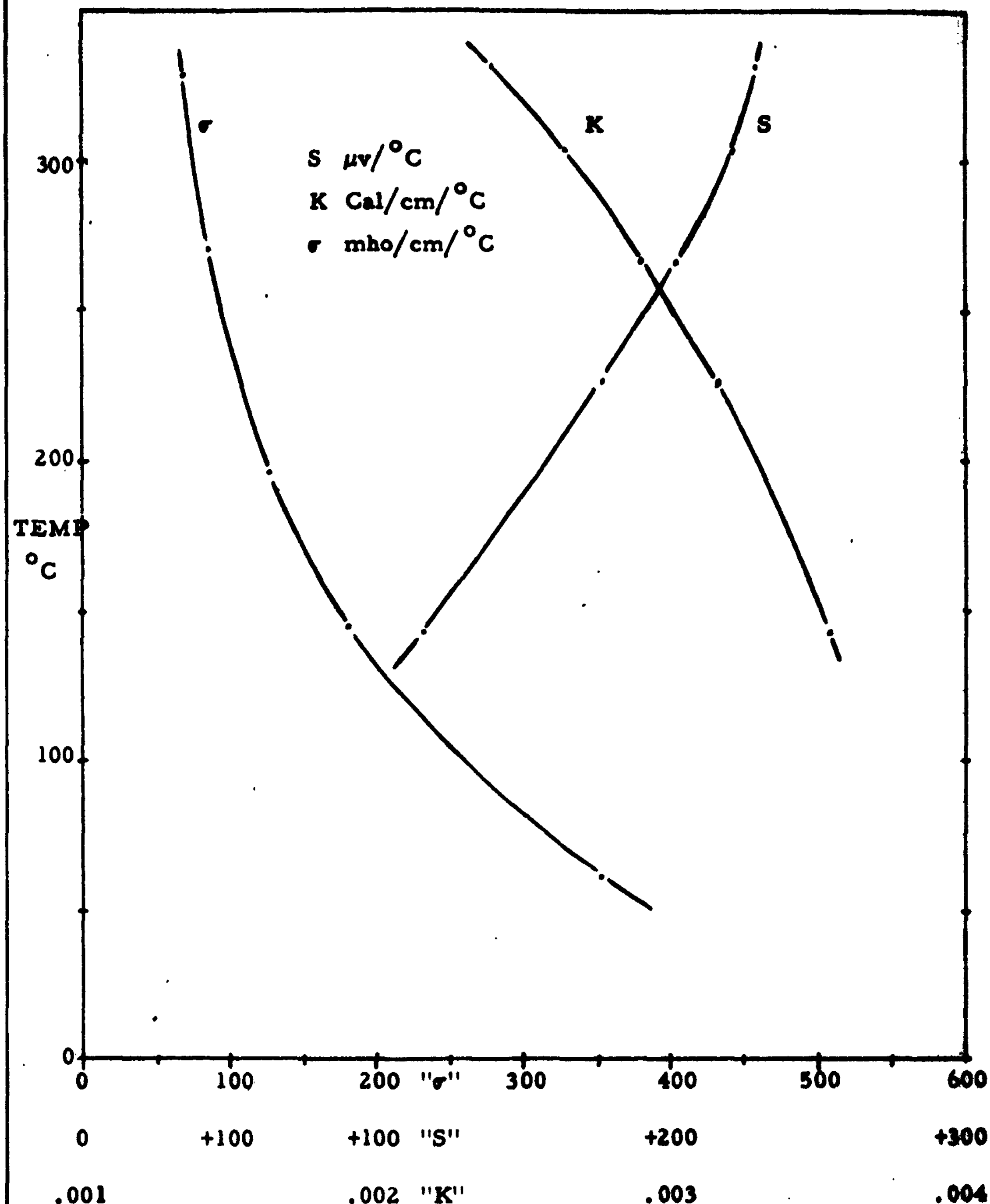
I - $P_bT_eS_e$

Figure #1



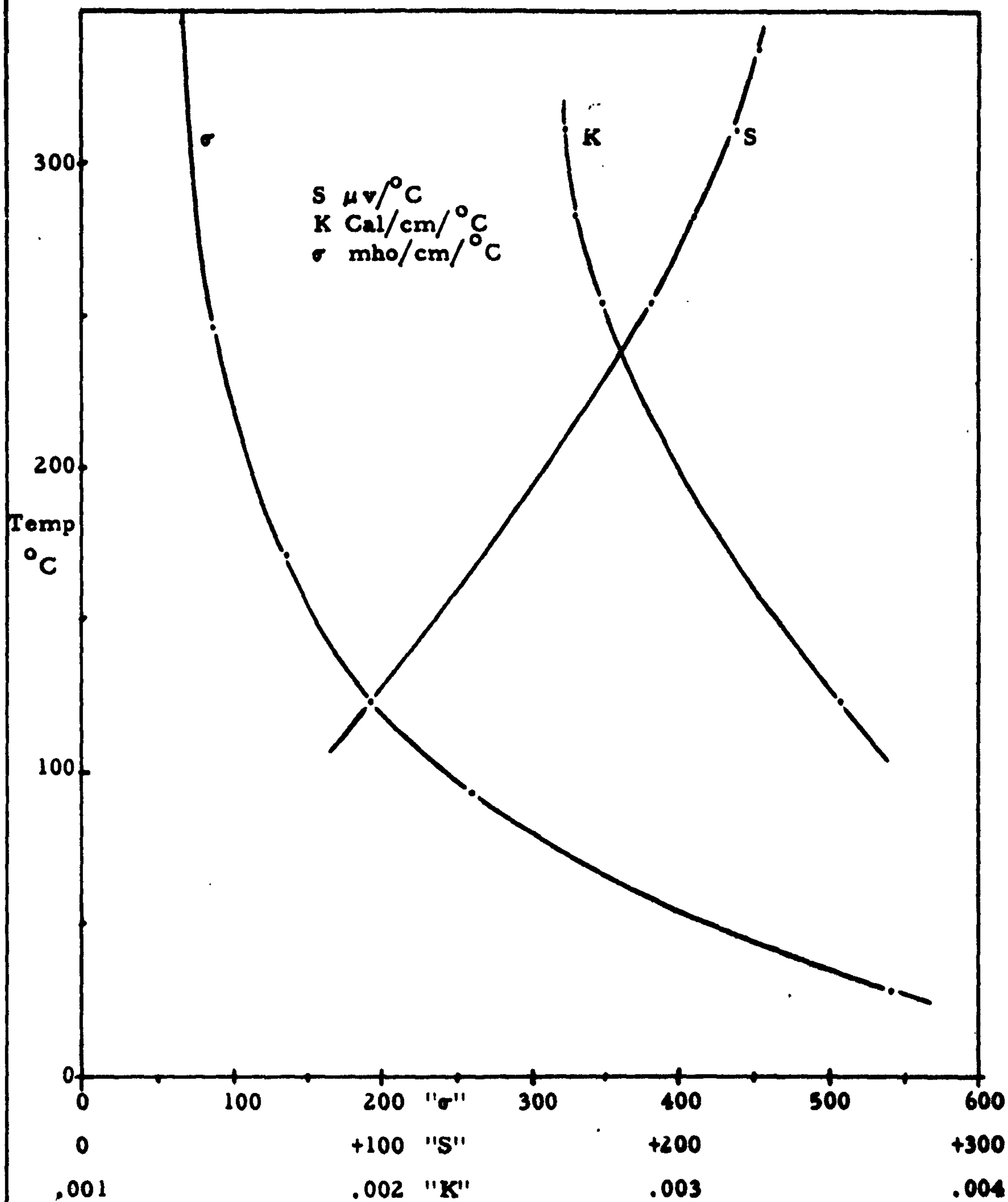
Lead Telluride N Type Sample #2
I - $P_bT_eS_e$

Figure #2



Lead Telluride P Type Sample #1
I - $P_bT_eS_e$

Figure # 3

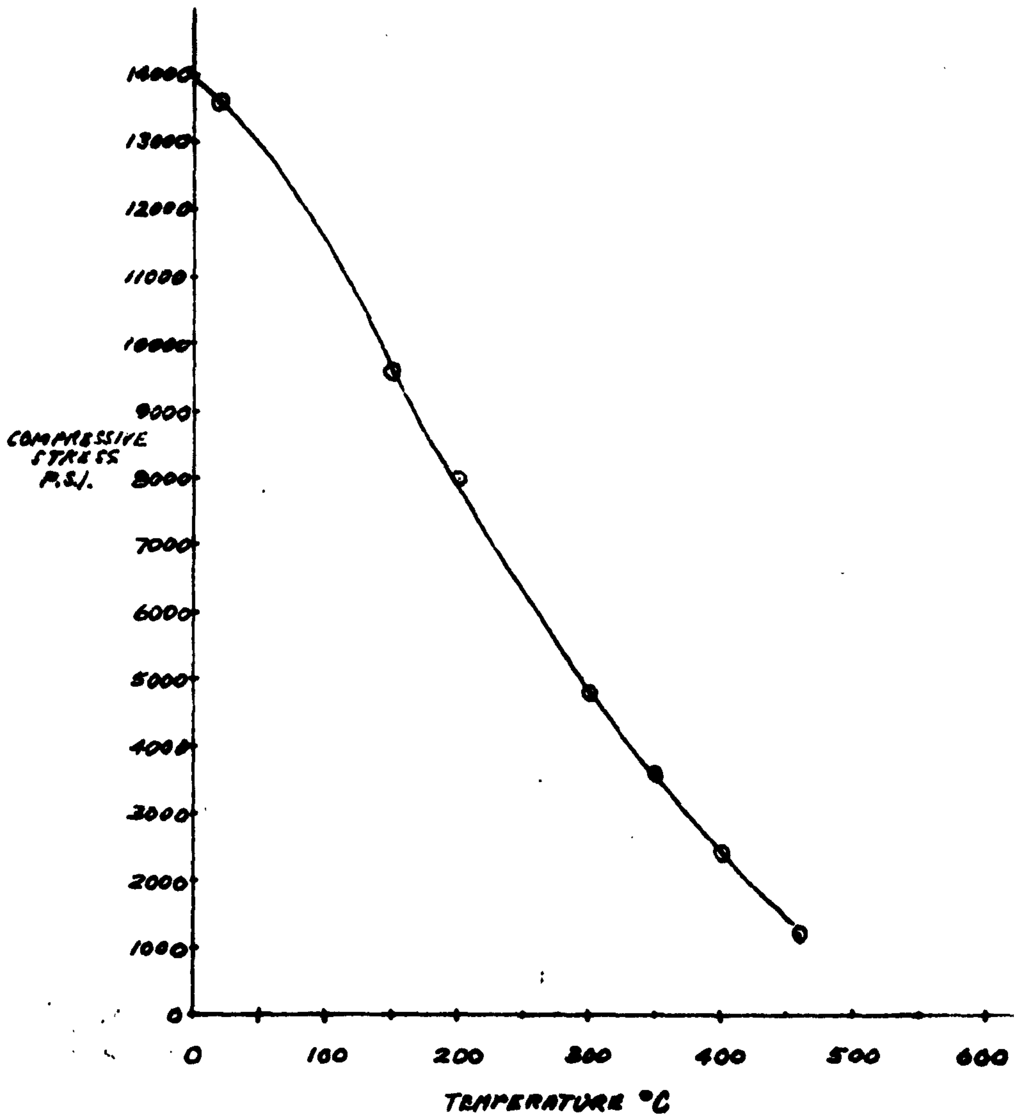


Lead Telluride P Type Sample #2
I - $P_bT_eS_e$

Figure #4

COMPRESSIVE YIELD STRENGTH OF PbTe

Figure 1 shows the short time compressive yield strength of a sample of lead telluride plotted as a function of temperature. The samples were taken from an engineering grade of lead telluride which was prepared at Servomechanisms/Inc. In a mechanical system, which is subjected to rapid changes of temperature, the short term thermal stresses are important. The compressive strengths here shown are those which are approached by the process of creep in a sample which has been subjected to stress at the indicated temperatures for not more than five minutes. These results were obtained by compressively loading a cylindrical column. This column was $\frac{1}{2}$" diameter and 1" long and fabricated by cold pressing at 56,000 psi followed by a heat treatment at 400° and 800 psi.



TYPICAL COMPRESSIVE YIELD STRESS (SHORT TIME)

LEAD TELLURIDE
COLD PRESSED AND HEAT TREATED

Figure # 1